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Iron Tannage

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BY

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To ALLEN ROGERS to whom the author owes his first interest in tanning this work is dedicated.

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IRON TANNAGE.

Section I. General Discussion.

As early as the latter half of the eighteenth century iron salts as tanning agents were proposed and experimented upon. From that time on attempt after attempt was made to obtain a satisfactory tannage with iron, but without material results. Different experimenters took up the matter with renewed enthusiasm, each cherishing a hope of thereby revolutionizing the tanning industry, but plants running on such processes were unsuccessful. When it is considered that next to alum, iron compounds were among the first inorganic salts introduced for mineral tannage, it may be realized how far iron tannage has fallen behind that of chrome and even of alum tannage at the present time. Diversified reasons have been given by different investigators to account for the unsatisfactory products obtained. No doubt, while some of these represent true causes responsible for the failure, much is due to a lack of understanding of the peculiar properties of the iron salts rather than to the intrinsic character of iron. It has been our object to make a study of iron tannage and to determine wherein the difficulties lie and how they may be met.

True to the general trend of the Periodic Table, aluminum with the lowest atomic weight is the most acidic, while iron having the highest atomic weight is the most basic, with chromium lying in between.[1] This accounts for some of the differences in the behavior of the three elements as tanning agents. But there seem to be, as far as the tanning properties are concerned, more fundamental differences, not in degree but in kind, which should be ascribed to their distinct properties as individual elements. For instance, both iron and alum tanned leathers do not resist boiling temperature, whereas chrome tanned leather is not affected unless it is subjected to boiling continuously for a considerable length of time.

Some investigators seem to have worked along the idea that the basic ferric sulphate corresponding to the formula $Fe(OH)SO_4$ is the compound in the liquor that brings about tanning, and

[1] See Stieglitz, "Quantitative Chemical Analysis," Vol. I, p. 195 (1919).

have striven to produce such a basic ferric salt liquor for this purpose. This is too basic for a sulphate liquor, although ferric chloride liquor can stand a higher basicity than this. Ferric sulphate in solution corresponding to this degree of basicity is not stable and the hydrated ferric oxide, $Fe_2O_3.xH_2O$, a fine yellow crystalline precipitate, will invariably separate out within a short time, even when the liquor is not diluted. If the liquor is diluted, turbidity is almost instantaneous with a rapid separation of the light yellow precipitate. To produce a good tannage with iron, the basicity of the liquor employed is found to be considerably less than this in the case of the sulphate and the range between which the basicity may vary is rather narrow. Symbolically the salt in the ferric sulphate tan liquor may be represented by $Fe_2(OH)_x.(SO_4)_y$ where x has a value between 1 and 1½ and y between 2½ and 2¼, but there is no definite formula assignable, as there is no sharply defined chemical compound and, besides, when it comes to neutralization, the iron that is fixed in the pelt is of a highly basic character. But any attempt to bring about the formation of such a basic salt as is represented by $Fe(OH)(SO_4)$ invariably causes a precipitate of $Fe_2O_3.xH_2O$. This $Fe_2O_3.xH_2O$ is entirely inert and we can not expect to obtain a tannage from it any more than from a precipitated $Cr_2O_3.xH_2O$ if such is produced in the chrome liquor from the use of too much alkali. The oft reported "hard and brittle leather" may be simply due to improper tannage from the presence of much precipitated $Fe_2O_3.xH_2O$. The difficulty with the iron liquor, then, is that the ferric salt, particularly the sulphate, is very readily hydrolyzed and that, what is still worse, upon hydrolysis the ferric hydroxide seems to pass through the colloidal range so rapidly that it is soon flocculated or coagulated as a light yellow crystalline substance $Fe_2O_3.xH_2O$. This will be appreciated when it is seen that $Al(OH)_3$ upon hydrolysis remains in the colloidal realm for a considerable time, and when finally separated out from the solution it does not readily become dehydrated as $Al_2O_3.xH_2O$. The same is true of $Cr(OH)_3$ from a chromic salt solution, and even more pronounced.

Another difficulty is that ferrous iron in solution, though easily partially oxidized is rather difficult to be completely oxidized. To effect a partial oxidation is one thing, but to oxidize completely all

the ferrous iron in solution to the ferric state seems quite another. Oxygen from the air will partially oxidize some ferrous iron in solution to the ferric state, but it never is able to oxidize it completely, except in alkaline solution. Perchloric acid, another oxidizing agent, oxidizes iron in solution partially but complete oxidation is quite difficult. With I_2, complete oxidation is impossible, although a small amount of FeI_3 is obtained. There is normally always an equilibrium between the ferrous iron and the ferric iron in solution. To shift the equilibrium to completion requires a much higher potential which is only secured by using a powerful oxidizing agent, or for the same oxidizing agent a higher concentration of this. The equilibrium ratio is

$$\frac{(Fe^{II})}{(Fe^{III})} = 10^{17} \text{ [1]}$$

Thus, a small concentration of ferric iron present in solution is normally sufficient to set up an equilibrium and it takes a considerable potential to shift the equilibrium to the ferric end. This consequently calls for the presence of some excess of a powerful oxidizing agent to prevent any of the ferric iron from being again reduced. Complexities result from the fact that iron is capable of existing in two different states, of which the ferric state is the one that possesses the tanning property and this gives rise to one of the great difficulties in iron tannage.

In the case of aluminum the problem is simpler, as aluminum does not exist in a state other than the trivalent, and it has little or no tendency to be flocculated into a similarly dehydrated $Al_2O_3.xH_2O$ compound in the solution.

As to chromium the condition is, on the other hand, decidedly favorable. For, while chromium does exist in other states, notably as CrO_4^{--}, or $Cr_2O_7^{--}$, it would take an excessively high oxidation potential to cause it to go to the chromate state, except in an alkaline solution, which is not the case with the chrome bath. Hence to all intents and purposes chromium under such conditions can be said to possess only one state of oxidation, *i. e.*, Cr^{III}, as is also the case with Al. Further, tanning conditions are far more favorable to reduction than to oxidation. The protein

[1] See Stieglitz, "Quantitative Chemical Analysis," Vol. I, pp. 270-275 (1919).

bodies in the hides and skins, the woody material of the drum or paddle, and the metallic joints of the apparatus all possess distinct reducing properties. Ferric salt in the liquor which is so susceptible of reduction is always reduced to a greater or less degree, as can be easily proved by testing the spent liquor with potassium ferricyanide solution after the tanning operation. In this connection it can not be too strongly emphasized that the tan liquor should not be left in contact with a wooden or iron container unnecessarily, and should not be introduced into the drum until the tanning operation is ready to begin. Much trouble has been traced to the iron liquor being materially reduced and converted to the ferrous state during the progress of tanning. For chrome tannage, this condition is exactly what we desire as chromium is to be kept at its lower state of oxidation, namely the chromic state.

From the above it is clear why there are added difficulties in the case of iron tannage. It is necessary, first of all, to convert the ferrous iron to the ferric state *completely*, then to keep it in this ferric state throughout the tanning operation under adverse conditions, and to prevent the separation of any hydrated ferric oxide, $Fe_2O_3.xH_2O$, by adjusting the proper acidity in the liquor employed.

Section II. History of Iron Tannage, Including Recent Work.

Attempts to use iron salts as tanning agents date back to the time when efforts were first made to find a substitute in the form of metallic salts for vegetable tannins. In the course of more than a century, efforts were repeatedly made and interest was continually revived to make iron tannage a commercial success, but without reward, in spite of the great promise that inspired such investigators to make a most determined effort. Within the last decade, partly on account of the Great War, new interest has been given to iron tannage, and the properties and behavior of iron salts as tanning agents are gradually becoming better understood.

The history of iron tannage begins from the latter part of the eighteenth century. Many of these early investigators are men who also helped to establish the present-day chrome tannage.

In the year 1770, J. Johnson,[3] an Englishman, patented a process of tanning using ferrous sulphate with an acid (sulphuric acid, hydrochloric acid or nitric acid). The pelt was tanned in three operations in the middle of which a vegetable tannin was used.

In 1794, Sam. Ashton,[4] another Englishman, recommended the use of a mixture of iron oxide and sulphuric acid, calcined iron ore or iron ochre with pyrites, copper ore, and zinc for tanning. The duration of tanning was given as from five to seven weeks. For calfskins some alumina was also added.

In 1805, Sigmond Hermbstadt[5] in his book on leather tanning explained that solutions of metallic salt baths had similar action on the pelt as the oak tannins. Among other salts he mentioned the red iron sulphate, in which not only the grain of the pelt was affected, but the pelt was virtually converted into leather if soaked in it for some time. He prepared his iron tan liquor by heating ferrous sulphate to a dry yellow substance which was dissolved

[3] *Handbuch der Chromgerbung*, Josef Jettmar, p. 133 (1900); also *Die Chromgerbung*, J. Borgmann, p. 6 (1902).

[4] *Ibid.*

[5] "Le Tannage au Fer," *Le Cuir*, Josef Jettmar, June 15, 1919

in twenty times its volume of boiling water, and on cooling, the clear yellow-red solution decanted for use. He also treated iron oxide with acetic acid, or oxidized ferrous sulphate with concentrated nitric acid or with a mixture of concentrated nitric acid and sulphuric acid. Sole leather as well as upper leather could be made in this way but the leather obtained was detanned in contact with water.

In 1842, d'Arcet,[6] a Frenchman, tanned the hides in a ferric sulphate solution but the sulphuric acid set free gradually destroyed the hides. In the same year, Julius Bordier,[7] of London, patented a process (British Patent 9,219, 1842) of oxidizing ferrous sulphate with nitric acid and sulphuric acid, and with manganese dioxide and sulphuric acid. It was said that he had attained some success.

In 1853, Hylten Cavalin,[8] employed for tanning, liquor containing 10 pounds of dichromate of potash and 20 pounds of alum in 180 pounds of water. The hides were tanned in this liquor for four days, and were next placed in a 10 per cent. ferrous sulphate solution for twelve hours with frequent stirring. The acidity relation of these two liquors was not properly adjusted and the iron was not completely oxidized. The leather obtained was hard and brittle.

In 1855, Rene de Kercado Molac and Jean Daniel Friedel,[9] both of Strasbourg, France, patented a process whereby the hides were tanned in a basic ferric sulphate solution which was later neutralized with metallic oxides, such as ferric oxide, alumina, and zinc oxide to remove the sulphuric acid liberated. They prepared the liquor with ferrous sulphate, manganese dioxide and sulphuric acid, and added to the liquor ferric acetate in varying proportions. A. E. L. Bellford, of London, patented their process in England. In this British patent (January 12, 1855) it was stated that the leather treated by other mineral processes is "liable to tear in length of time on account of the great quantity of acid remaining in the leather corroding the animal fibres."

[6] "Leather Industry," A. M. Villon, trans. by F. T. Addyman, p. 189 (1901).

[7] See also "The Arts of Tanning," Campbell Morfit, p. 396 (1852).

[8] "The Arts of Tanning," Campbell Morfit, pp. 397-401 (1852).

[9] Compare "Handbuch der Chromgerbung," Jettmar, p. 137.

Dr. Frederich L. Knapp, Professor of the Polytechnic School of Brunswick, Germany, made a thorough, scientific investigation on these mineral tannages and published the results in "Die Natur und das Wesen der Gerberei und des Leders" (Munich, 1858), and also in an article, "Über Gerberei und Leder," in Dingler's Polytechnische Journal, Vol. 181, p. 311 (1866). He made a satisfactory explanation of the tanning action. He had in mind the possibility of reducing the length of time needed in the vegetable tanning process and eliminating the costly materials such as egg-yolk and flour used in alum tannage. He recognized the plumping effect upon the hides by the acid liberated during tanning and the stiff and brittle character of the leather obtained. He recommended neutralizing the tan liquor during the progress of tanning with sodium carbonate or caustic soda and pointed out the advantages in so doing, namely, that the hides were more richly tanned, that the harmful acid effect was prevented, and that a neutral electrolyte NaCl (in $FeCl_3$ liquor) was produced in the tan liquor. His English patent (British Patent 2,716, 1861, through John H. Johnson) covered iron, chrome, manganese, and other metallic salts in combination with fatty acids to form insoluble metallic soaps so that the iron in the pelt might not be washed out. He also mentioned the use of similarly insoluble silicates of aluminum and alkaline earths. According to his patent (German Patent No. 444, 1877) he prepared his liquor by adding nitric acid in excess to oxidize completely a boiling ferrous sulphate solution when brown nitrogen dioxide (NO_2) fumes were seen. After all iron was oxidized he introduced more ferrous sulphate into the resulting solution as long as NO_2 fumes were evolved. The liquor after evaporation becomes a varnish-like liquid. Judging from this description his liquor must have been too alkaline through the loss of the nitric acid by boiling. In his additional patent (German patent No. 10,518, 1879) he used instead of the nitric acid, sodium nitrate and sulphuric acid for oxidation. This method is far more economical and involves no danger of losing the acid by heating so that the acidity of the resulting liquor is under control. Furthermore, a neutral salt, Na_2SO_4, is produced in the tan liquor.

In 1864, F. Pfannhauser[10] obtained a patent for the preparation

[10] "Manufacture of Leather," Chas. T. Davis, p. 290 (1897).

of a basic ferric sulphate solution and its use in tanning. He roasted ferric sulphate to a red heat with continuous stirring until it was reduced to a red powder which was then thrown into water while still hot. Most of this powder was said to be dissolved. The suspension was allowed to settle and the supernatant liquid drawn off for the preparation of tan liquors of varying strength. The skins were tanned countercurrently and, when tanned, placed in a soap solution.

In 1877 Paesi[11] proposed to use a ferric chloride solution together with salt at 20° C. in the ratio of 100 parts of water to ten parts of $FeCl_3$ and five parts of salt.

In 1881, E. Harcke obtained a German patent, No. 19,633, according to which the pelt for making sole leather was treated with a mixture of a resinous body (such as rosin), coal tar creosote, or carbolic acid, and an alkali, in water, until thoroughly penetrated. The pelt was then tanned, first in an aluminum salt solution and then in a ferric chloride solution, or other ferric salt solution. For making upper leather the hides were previously limed and if softness and porosity were desired, the rosin could be omitted.

In 1881, W. Eitner[12] patented a process (Austrian Patent No. 6,775) using a mixture of a basic chromic sulphate and ferric sulphate solution. This process was used in Graz, Austria, and the product known as "Patentleder, Marke Elefant." By changing the ratio of the chromic salt to the ferric salt different gradations of color—from yellow (of the iron) to gray (of the mixture) and to green (of the pure chrome)—were obtained. When a mixture of the ferric and chromic salts was used, the leather was colored black with logwood alone; when chromic salt alone was used, the leather was colored black with logwood and an iron "striker." When yellow color was not desired in the product, chromic salt alone was used for tanning. Leather obtained in this way was stuffed, after sammying, with mixtures of train oil, castor oil, stearin, tallow, mineral oil, etc., with soda bicarbonate, soap, borax, casein, etc., as emulsifying agents.

[11] "Leather Industry," A. M. Villon, trans. by Addyman, p. 189 (1901).

[12] "Die Chromgerbung," J. Borgmann, pp. 49-54 (1902); also "Handbuch der Chromgerbung," Jettmar, p. 151 (1900).

In 1886, John W. Fries, of Salem, North Carolina, patented a process of tanning (U. S. Patents Nos. 343,160 and 343,167) using ferrous carbonate (or ferrous sulphate), sodium carbonate (or sodium bicarbonate) and sulphuric acid. The skins were tanned first in a dilute liquor for two or three days and then in a more concentrated liquor for the same length of time. A small amount of sugar might be added. After the tanning operation the skins were hung in the air to get the iron oxidized. For currying, he used tallow with a paraffin oil, lard, or cotton seed oil, and later, in his patent No. 343,167, he recommended an alcoholic solution of castor oil.

In 1892, Paul F. Reinsch, Erlangen, Bavaria, patented a process (German Patent No. 70,226) using a liquor prepared by mixing 10 kg. $FeCl_3$ dissolved in 40 l. of water with 4½ kg. crystalline Na_2CO_3 dissolved in 20 l. of water, thus yielding a dark brown solution. He called it ferric chloride-sodium chloride liquor, which he used for making different kinds of leather either alone or in combination with alum-sodium chloride tannage. In 1912 he obtained another German patent, No. 265,914, on the use of ferric chloride and magnesium carbonate. He prepared the liquor by dissolving 1 kg. ferric chloride in 4 l. of water to which was added a suspension of 225 g. $MgCO_3$ in a liter of water. To this mixture he added a solution of 8 per cent. aluminum chloride. Evidently his idea is to bring about the required basicity by $MgCO_3$. The $AlCl_3$ present is probably meant to help keep the basic ferric chloride in solution.

J. Bystron and Karl Baron von Vietinghoff obtained a number of German patents, Nos. 255,320, et seq., in 1911, a British patent, No. 13,952 in 1912, and two U. S. patents, No. 1,048,294 in 1912 and No. 1,061,597 in 1913. They employ nitrogen dioxide, NO_2, and nitrogen trioxide, N_2O_3, for the oxidation of iron. The nitric oxide, NO, from the oxidation reaction is collected and reoxidized by contact with fresh air to NO_2 and N_2O_3, which gases are used over again for oxidation. They thus proposed to utilize the NO_2—NO—NO_2 cycle, making the oxides of nitrogen virtually catalytic agents for the oxidation of iron. In the British patent, No. 13,952, they observed considerable precipitates formed in the tan liquor and on the skin. According to them, the presence of large quan-

tities of an acid causes the formation of a highly acid and not completely insoluble iron oxide in the skin so that the leather made is brittle and can not be stored. In this patent and also in the U. S. patent No. 1,048,294 he proposed placing the skin in a ferrous salt solution and oxidizing the ferrous iron by passing in NO_2 gas from outside or by liberating HNO_2 from a nitrite added to the liquor. Thus they attempt to combine the oxidation reaction and the tanning operation in a single procedure. It is true that HNO_2 (from a nitrite and an acid) has sufficiently high oxidation potential to oxidize ferrous iron to the ferric state, but in order to oxidize all the ferrous iron into the ferric state completely, the presence of much acid in the solution and of an excess of the oxidizing agent is needed. If the oxidation by HNO_2 or oxides of nitrogen is to take place simultaneously with tanning operation at the low acidity necessarily present in the tan liquor, probably there will be much difficulty in getting all of the ferrous iron completely oxidized. Bystron in the U. S. patent No. 1,061,597 patented the use of a neutral alkali salt such as Na_2SO_4 or NaCl for treating the iron-tanned leather. He claimed that by this treatment a more insoluble basic ferric salt of a light color is formed in the leather, thereby yielding a soft, elastic, and non-brittle leather.

O. Röhm in 1917 obtained British patents Nos. 103,827 and 104,338 on the combination tannage using formaldehyde and ferric chloride, or formaldehyde and a mixture of ferric chloride and chromic chloride or aluminum chloride. In his patent No. 103,295 (not accepted) he mentioned the use of ferric alum mixed with vegetable tannins to form iron tannate (ink) for tanning. In his patent No. 103,827 he recommended tanning with formaldehyde in sodium bicarbonate solution followed by a tannage with a ferric chloride solution, a mixture of ferric chloride and chromic chloride, a mixture of ferric chloride and aluminum chloride, a ferric chloride solution and then vegetable tannins, or a ferric chloride solution with an alkaline sulphide. He also mentioned the treatment of the skin with an iron precipitant, such as NH_3, alkalies, or alkaline salts; or phenols, naphthols, organic carboxylic acids, vegetable tannins; or soap, sulphide, polysulphide, and the like. He mentioned that the leather obtained would not become slippery in wet condition as is the case with a chrome

leather. In his patent No. 104,338 he stated that the aldehyde tannage could be advantageously used to follow iron tannage after neutralization or together with neutralization. When the aldehyde is introduced together with the neutralization after the iron tannage, there is, according to his observation, an advantage that the grain-drawing so common in a mineral tannage will be prevented. His thought seems to be along the line that since aldehyde tannage is carried on in an alkaline solution, the introduction of the aldehyde tannage after the iron will serve also as a neutralization operation to fix the iron in the pelt. We have tested this combination tannage and found the leather so obtained satisfactory. But since formaldehyde is a tanning agent by itself, to what extent the iron salt has contributed to the tannage is difficult to tell.

Emil Kanet[13] in his German patent No. 306,015 (1918) introduced an interesting feature in the mode of tannage. He derived the tanning action by the hydrolysis of a ferric salt. He treated the pelt at a low temperature with a ferric salt solution of such a basicity that it would be unstable at the ordinary temperature, and, after allowing the liquor to penetrate the pelt, raised the temperature to bring about hydrolysis. To illustrate, he placed the skins in a basic ferric acetate liquor containing from ½ to 2½ per cent. Fe_2O_3, preferably with the addition of some salt or other electrolyte such as sodium acetate. After the skins were penetrated by the tanning liquor he transferred them to a fairly concentrated salt solution at a temperature of from 45° to 60° C., or exposed them to heat in a warm chamber. The tanning action was completed in a short time but the stock was further laid aside for some time to fix the iron. The acetic acid set free under the influence of heat can be recovered from the skins by pressure. If a filling material such as flour is used with the tan liquor, it is, according to him, fixed in the leather with the basic ferric acetate. Other mineral salts such as chromic salt can be mixed with the iron. The advantage claimed is that at a low temperature a more basic ferric salt solution can be used and that the oxidizing activity of the ferric iron towards the skins is lessened.

[13] Compare also "Le Tannage au Fer," by J. Jettmar, *Le Cuir*, July 1, 1919.

W. Mensing in his Swiss patent No. 75,775 in 1918, recognized the ease with which ferric salt in solution is decomposed and mentioned the effect of ferrous iron upon the skin when the ferrous salt is present in the tan liquor. He recommended the use of an excess of an oxidizing agent and patented the use of a chlorate (Na, K, or Ba) as the oxidizing agent. He also recommended a preliminary treatment of the skin with borax or a basic aluminum or chromic salt solution for the use of a slightly more acid or neutral ferric liquor. According to his idea the tanned stock should not be washed with water but only wrung or pressed to get rid of the excess of the tan liquor. On drying, the stock is oiled with a mineral oil, paraffin or ceresin and then washed. To avoid reaction of the iron in the pelt with vegetable tannins he recommended fixing the iron by treating the leather with a slightly alkaline solution before vegetable retanning. He advocated the bleaching of the leather by detanning the surface layers by means of a reducing agent and then an acid. On the whole, his patent marks a better understanding of the properties of the iron tan liquor and the process of iron tannage.

Vittorio Casaburi,[14] in the articles, "Notes on the Tannage of Skins with Iron Salts," published the results from a series of his experiments, using a basic ferric sulphate solution (from the oxidation of ferrous sulphate with a mixture of nitric acid and sulphuric acid), a solution of a mixture of basic ferric chloride and sulphate (from the oxidation of ferrous sulphate by nitric acid and hydrochloric acid), a basic ferric chloride solution, and a basic ferric acetate solution. He employed a strength of iron liquor containing 1 per cent. Fe_2O_3 of the weight of the pelt in a little over four times the weight of water of the weight of the pelt. According to him 7.88 per cent. of Fe_2O_3 in the leather on the basis of the dry weight is sufficient to convert the pelt into leather. He stated that he had started with a tan liquor having such a basicity as to correspond to the formula $Fe_2(SO_4)_2(OH)_2$, but his iron and basicity determinations in the liquor showed that the liquor he used was more acid than this, the basicity of his first liquor (basic ferric sulphate) being only one-half of this value, and that of his second liquor (a mixture of basic ferric sulphate and chloride) less than a half of this value. We have

[14] *Le Cuir*, Aug. 1, Sept. 1 and Sept. 15, 1919.

found that a sulphate liquor having so high a basicity as to correspond to $Fe_2(SO_4)_2(OH)_2$ is too alkaline for use. Throughout the course of tanning he strengthened the liquor with fresh portions of the strong liquor. He drew a conclusion that the final basicity of the liquor was the same as that at the beginning of tanning—a conclusion that has not been confirmed by our experiments.

Section III. Investigation of Different Methods of Oxidation and Some Methods of Preparation of Iron Liquor From Copperas.

As the largest and cheapest commercial source of iron salts is in the form of the ferrous sulphate or "copperas," $FeSO_4.7H_2O$, this particular salt of iron naturally forms the starting point for the preparation of the tanning solutions. As the ferric salts are generally more expensive than the corresponding ferrous salts, economy demands that the iron tanning liquor shall be made from the ferrous salt—"copperas" in particular—rather than directly from a ferric salt purchased as such. Hence it is clear that a proper method of oxidation is essential to the preparation of this tanning liquor and constitutes one of the main factors in the economic aspects of iron tannage. Consequently it is worth while to devote some attention to the study of different methods of oxidation and of the value of different oxidizing agents from the tanning point of view. In this investigation, mostly qualitative, we have constantly kept in view three points, namely (1) the simplicity of the method by which oxidation can be carried out; (2) the character (acidity, etc.) of the liquor thus obtained in regard to the convenience for use; and (3) the cheapness of the chemicals employed. In the following there is given a brief summary of the properties and behavior towards ferrous sulphate solution of some of the more important oxidizing agents, although the study includes practically all of the ordinary oxidizing agents available.

Sodium Dichromate, $Na_2Cr_2O_7.2H_2O$.—Oxidation goes on in the cold and to completion (as tested with $K_3Fe(CN)_6$ solution) even in the absence of any acid added. There is a tendency for the ferric oxide, $Fe_2O_3.xH_2O$, to separate out. With a small amount of a mineral acid added no precipitate will be formed and the reaction is distinctly accelerated by the higher hydrogen-ion concentration.

$$Cr_2O_7^{=} + 6Fe^{++} + 14H^{+} \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

This method is an important one and embodies one mode of tannage found to give satisfactory results. It has several advantages: (1) that the oxidation reaction requires only a very low

hydrogen-ion concentration, so that the acidity of the liquor obtained is entirely in control; (2) that the oxidation potential is high and the oxidation reaction is completed very smoothly in the cold; and (3) that the waste product, Cr^{+++} salts left in the resulting liquor is itself a valuable tanning agent and constitutes what may be called a co tanning agent with the iron. Furthermore, a slight excess of the sodium dichromate in the liquor could effectively prevent any ferric iron from being reduced to the ferrous state in the course of tanning. In spite of the present high price of the dichromate, the process has merits of its own as will be presented in detail in a later section.

Sodium Chlorate, $NaClO_3$.—The oxidation by a chlorate $NaClO_3$ or $KClO_3$ in a cold solution does not occur without the addition of a mineral acid (HCl or H_2SO_4). On adding the acid the reaction takes place rapidly and goes to completion in the cold. The solution assumes a greenish-yellow color, probably due to some chlorine dioxide formed, ClO_2.

$$2NaClO_3 + HCl \longrightarrow 2NaCl + HClO_3.$$
$$HClO_3 + 6FeSO_4 + 5HCl \longrightarrow 2Fe_2(SO_4)_3 + 2FeCl_3 + 3H_2O.$$
$$3HClO_3 \longrightarrow H_2O + 2ClO_2 + HClO_4.$$

With a weaker acid, like acetic acid, oxidation takes place on heating, giving a red solution due to the formation of the basic ferric salt. Without any acid added the reaction can be brought about by heating, but $Fe_2O_3.xH_2O$ would then be thrown down. As the chlorate is rather expensive, especially the potassium chlorate, the process will not be economical, although W. Mensing advocated its use in his patent.[15]

Manganese Dioxide, MnO_2.—In the absence of any acid, no reaction takes place, MnO_2 being insoluble. On adding HCl, evolution of Cl_2 gas is observed and the solution turns yellowish, this being the characteristic color of the ferric chloride in solution.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2.$$

The reaction proceeds to completion in the cold.

If in place of HCl, H_2SO_4 is used, the yellow color does not develop. The reaction goes to completion only when a large

[15] Swiss Patent No. 75,775, Class 40, February 1, 1918.

excess of MnO_2 and H_2SO_4 is employed. A small but distinct amount of the permanganate is formed when all ferrous iron has been oxidized. Hence if MnO_2 is to be employed as the oxidizing agent, HCl rather than H_2SO_4 should be used. Molac and Friedel in 1855 prepared their iron liquor from ferrous sulphate with MnO_2 and H_2SO_4.

Nitric Acid, HNO_3.—1. *HNO_3* alone.[16] Dilute HNO_3 has scarcely any oxidizing action upon a dilute $FeSO_4$ solution in the cold. With somewhat more concentrated HNO_3 solution, a black coloration gradually develops due to the reduction of some HNO_3 to nitric oxide, NO, which unites with $FeSO_4$ to form the ferrous nitroso compound $FeSO_4.NO$. The black color deepens on warming and persists even on boiling if the concentration of the HNO_3 in the solution is not high enough to effect the oxidation. With the addition of more HNO_3 or with an increase in the concentration of the HNO_3 due to the loss of water by prolonged boiling, complete oxidation finally takes place and all of the nitroso compound is decomposed. The solution then boils violently, brown fumes of nitrogen dioxide, NO_2, being given off. During the evolution of the gas the temperature of the solution falls 4° or 5° C. The amount of HNO_3 required for complete oxidation depends largely upon the concentration rather than the absolute quantity of HNO_3 present. Starting with a saturated solution of $FeSO_4.7H_2O$ (one part of $FeSO_4.7H_2O$ in about one and a half parts of water by weight) and using 1.42 HNO_3, a considerably less amount of the HNO_3 need be employed, but 25 per cent. of 1.42 HNO_3 of the weight of $FeSO_4.7H_2O$ taken is found to be the working minimum under such conditions. Although complete oxidation can still be brought about with a less quantity, say 20 per cent., the liquor obtained becomes too alkaline and has a muddy appearance, due to the separation of the ferric oxide. This can be readily understood when we see that when the ferrous salt is oxidized to the ferric salt, the solution becomes less acid and the greater part of the HNO_3 used simply goes to furnish the necessary acidity (see paragraph under $HNO_3 + H_2SO_4$ below). Some HNO_3 is lost by boiling.

[16] This method was used by Knapp, but the liquor he prepared yielded much $Fe_2O_3.xH_2O$.

The oxidation of the ferrous iron to the ferric state by HNO_3 in the *cold* can only approach completion when a very large excess of the concentrated HNO_3 is added to a concentrated ferrous sulphate solution. Consequently boiling is a necessary operation which makes the process less simple, as boiling nitric acid solution requires a special container to resist corrosion.

2. *$HNO_3 + H_2SO_4$.* As was said above, the oxidation of the ferrous solution to the ferric state renders the solution more alkaline, so that an acid must be added to prevent any ferric salt from being hydrolyzed and precipitated. If H_2SO_4 in the required amount is added to supply the acidity, the HNO_3 needed can be cut down from 25 per cent. of the weight of the $FeSO_4.7H_2O$ to 9.5 per cent.. Thus—

$$3FeSO_4.7H_2O + 4HNO_3 \rightarrow 3Fe(NO_3)(SO_4) + NO + 2H_2O$$

theoretically requires 30.2 per cent. HNO_3 of $FeSO_4.7H_2O$.

$$6FeSO_4.7H_2O + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

theoretically requires only 7.55 per cent. HNO_3 of $FeSO_4.7H_2O$. As HNO_3 is far more expensive than H_2SO_4 this method is more economical.

3. *$H_2SO_4 + NaNO_3$.*[17]—With a saturated ferrous sulphate solution (1 part $FeSO_4.7H_2O$ in about 1½ parts of water) and with 25 per cent. of H_2SO_4 and $NaNO_3$ each in excess calculated according to the following reaction,

$$6FeSO_4.7H_2O + 4H_2SO_4 + 2NaNO_3 \rightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 2NO + 4H_2O,$$

the reaction goes on very smoothly by continued boiling. The resulting liquor, thick like a syrup and dark red in color, has a specific gravity as high as 1.50—1.55 and contains iron as $Fe_2(SO_4)_3$ from 40-45 per cent. As Chile saltpetre, $NaNO_3$, is much cheaper than HNO_3, this method is still more economical. Furthermore, the Na_2SO_4 formed in the liquor cuts down the amount of NaCl needed for tanning. Taking 4 5 per cent. as the normal figure for NaCl used on the weight of the pelt, this saves about 25 per cent. of NaCl required.

4. *$HNO_3 + HCl$*, aqua regia. The reaction starts in the cold. When only a small quantity is added to the ferrous sulphate solu-

[17] This method was used by Knapp, but the details differ.

tion the black color of the nitroso compound is observed, but on further addition of aqua regia the nitroso compound is decomposed and the reaction goes to completion, although the end-point is not very permanent. The solution on standing gradually assumes a golden yellow color due to some hypochlorous anhydride Cl_2O formed. The main reactions seem to be—

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O,$$
$$NOCl + Cl_2 + 3FeSO_4 \longrightarrow NO + FeCl_3 + Fe_2(SO_4)_3,$$

although other oxidizing agents such as HNO_2 and $HClO$ are also formed. The proportion of 1.20 HCl to 1.42 HNO_3 is 3 -3.5 to 1 by volume of the concentrated solutions.

The oxidizing power of aqua regia seems to be greater than that of the concentrated HNO_3 alone, but some assert that there is no difference in oxidation potential between aqua regia and concentrated nitric acid.[18] As aqua regia is difficult to handle and rapidly corrodes the container, this method of oxidation is neither economical nor simple.

It will be noticed that with the possible exception of $HNO_3 +$ HCl, all methods involving oxidation by HNO_3 in some form require a boiling temperature. This constitutes a very unfortunate feature. There are, however, some distinct advantages in the case of $NaNO_3 + H_2SO_4$, *viz.*, (1) that the materials used are cheap; (2) that a very concentrated liquor can be obtained, and (3) that with a proper amount of H_2SO_4 employed the liquor obtained is stable and there is no danger of deterioration on storing.

Chlorine Gas, Cl_2.—The oxidation by chlorine is very smooth and simple. The reaction starts in the cold and goes to completion when the gas is passed in under a small pressure and when efficient stirring is maintained. The reaction furnishes its own acidity and in the right proportion.

$$Cl_2 + H_2O \longrightarrow HCl + HClO.$$
$$HClO + FeSO_4 + HCl \longrightarrow FeCl.(SO_4) + H_2O.$$

The process is very efficient and incurs practically no loss of Cl_2 if two or three units are connected in series and the solutions treated countercurrently. Iron liquor obtained by this method is

[18] Moore, "Aqua Regia," *J. A. C. S.*, p. 1091 (1911), and "Aqua Regia II," *J. A. C. S.*, p. 33 (1913).

of course saturated with Cl_2 and so contains a slight excess of it, but this is indeed an advantage for it prevents the ferric salt from being reduced again and also enables the liquor to be kept in storage without any danger of deterioration, *i. e.*, either $Fe_2O_3.xH_2O$ separating out or some ferric salt changing to the ferrous. As liquid chlorine now can be obtained in large quantities and at a reasonable cost, there is in it much to recommend from a commercial standpoint.

Bleaching Powder, CaCl.ClO.—This method is one of the first used by us in this research. The oxidation goes on in the cold. With large excess it is possible to oxidize completely the ferrous iron without adding any acid, in which case a precipitate of $Fe_2O_3.xH_2O$ is liable to come down. With a weak acid present, *e. g.*, acetic acid, the reaction is accelerated, and with a mineral acid it goes to completion readily. $CaSO_4.2H_2O$ is thrown down. $Fe_2O_3.xH_2O$ is more readily separated from this liquor probably due to the greater coagulating influence of the divalent radicals. The bleach suspension itself reacts alkaline so that the addition of an acid is rendered more necessary. As the oxidizing agent is really HClO, there is no advantage in using this material over liquid chlorine and the cost is greater for the chlorine content in this form. The bleach, however, can be used to advantage in connection with iron tanning processes (to be described in later Sections).

Sodium Nitrite, $NaNO_2$.—Unlike $NaNO_3$, oxidation begins in the cold, but basic ferric salt would be precipitated when no acid is added. On adding an acid (HCl or H_2SO_4) the red precipitate redissolves and nitrogen oxide gases are rapidly given off.

$$2HNO_2 \longrightarrow H_2O + N_2O_3.$$
$$N_2O_3 \rightleftarrows NO_2 + NO.$$

The reaction then goes to completion in the cold when an excess of $NaNO_2$ is present. With acetic acid the reaction can also go to completion giving a colloidal suspension. As the $NaNO_2$ solution reacts alkaline, the addition of an acid is all the more necessary. The oxidation potential of HNO_2 is lower than that of HNO_3,[19] although the latter produces no appreciable oxidation in the *cold*, especially when the solution is dilute. Since HNO_2

[19] Ihle, *Z. f. phys. Chem.*, Vol. 19, p. 577 (1896).

is unstable and is decomposed readily, the loss of HNO_2 through decomposition and volatilization is very great. Bystron and Vietinghoff[20] patented a cyclic process to collect these gases, oxidize them all to NO_2 by air, and use the gas again for oxidation. It is probable that such a method can not be carried out in practice without undue complications.

Hydrogen Peroxide, H_2O_2.—The oxidation starts in the cold, but does not go to completion without a large excess. Even with a large excess the end-point is not stable. $Fe_2O_3.xH_2O$ is thrown down on standing for a few minutes. The solution is red, due to the basic ferric salt formed. If an acid (HCl or H_2SO_4) is added the color of the solution becomes yellow and the reaction goes to definite completion, giving a more permanent end-point.

$$H_2O_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O.$$

As H_2O_2 cannot be obtained cheaply, at least at present, its use will not be commercially practicable.

Potassium Perchlorate, $KClO_4$.—The oxidation starts only on warming when no acid is added, but the solution then becomes turbid. On adding an acid, the turbidity clears up but the reaction does not go to completion even when the solution is heated to boiling. Thus contrary to what one might suppose, the oxidation potential of the perchloric acid is lower than that of the chloric acid.

Oxygen From the Air.—The oxidation of the ferrous sulphate by air oxygen would be a very cheap method if it could be brought about rapidly enough. Fine bubbles of air are passed through the ferrous sulphate solution, but the reaction is too slow, only 6 per cent. being oxidized at the end of four hours. At an elevated temperature, 80°-90° C., the reaction is more rapid, but even then only 12 per cent. is found to be oxidized in four hours. 10 per cent. concentrated H_2SO_4 of the weight of the $FeSO_4.7H_2O$ in the solution (1 part $FeSO_4.7H_2O$ to 2 parts water) should be present, otherwise ferric oxide would be precipitated. The ordinary catalytic agents, such as the mercuric salt (5 per cent. $HgCl_2$) and the phosphate (5 per cent. Na_2HSO_4) do not seem to help. Ozonized air, or air led through an electric ozonizer, would do better, but would be expensive.

[20] German Patent No. 255,320 (1911) and a number of patents following.

Anodic Oxidation. Oxidation by electrolysis seems to have some possibilities. The anode is best made of lead but the cathode can be lead, graphite, copper, or even iron. These materials have been tried. Lead and graphite as cathodes are inert in the acid (H_2SO_4) solution and are found to be suitable. Copper cathode is not attacked by the acid when the cells are running, but when the current is stopped it is attacked by the acid with the aid of atmospheric oxygen, thus contaminating the electrolyte. An iron cathode can be used to advantage as it is of the same material as the liquor is composed of. As the cathode environment is a reducing one, a diaphragm such as porous earthware, asbestos felt, or electro-filtrose should be provided to separate the cathode portion from the main electrolyte. This arrangement prevents the hydrogen gas evolved at the cathode from mixing with the main electrolyte. The cathode chamber need not be large, and a capacity of about one-fifth or less of the volume of the main electrolyte is sufficient. The cathode solution can best be a plain H_2SO_4 solution and should be maintained at a higher level than the body of the electrolyte to prevent diffusion of much iron into the chamber. It is found that the H_2SO_4 concentration inside this chamber should be maintained high, about two or three times as high as in the main electrolyte, otherwise some iron might be plated on the cathode. The electrolyte is made by dissolving copperas in about twice its weight of water and adding 15 per cent. concentrated H_2SO_4 of the weight of copperas taken. As, generally speaking, the oxygen over-voltage is low[21] oxygen gas is easily caused to be discharged at the anode, resulting in low current efficiency. To prevent this, the anode current density must be low, *i. e.*, the anode surface must be large. It is found that with the anode current density of 0.20—0.40 amperes per square decimeter for a liquor containing 25—40 per cent. of copperas, the over-all current efficiency is as high as 70—75 per cent., even when there is no circulation or stirring in the main electrolyte. With good circulation or stirring and with a concentrated electrolyte (30—40 per cent. $FeSO_4.7H_2O$) a higher current density can be safely employed without any danger of the discharge of oxygen gas at the anode. The cell takes a voltage of 2.4—3.0 volts depending upon the distance between the electrodes, the condition of the

[21] See Allmand, "Applied Electrochemistry," p. 144 (1920).

diaphragm, the concentration of the electrolyte and its temperature, but with the cells running properly and with the electrodes about 4 inches apart, this terminal potential drop should not be much over 2.6 volts under normal conditions. The back E. M. F. is approximately 2 volts. Oxidation can go to completion by this method, but the end-point is not quite permanent. As each cell on the average takes less than 3.0 volts, there can be connected in series on the 120 main about 40 cells. In this way, the method compares favorably with the cheapest chemical methods. The disadvantage seems to be that considerable amount of $Fe_2O_3.xH_2O$ is thrown down as sludge in the cells and the cells need close attention and regulation in regard to the acidity in the cathode chamber, proper conditions of the diaphragm, etc., otherwise secondary reactions might set in and the cells fail to function properly. It is found that the lead anode is oxidized only after all iron has been oxidized.

From the above brief description it will be seen that, to produce such a cheap product as the ferric salt, many of the costly and rarer oxidizing agents will find no place. Considerations of the different factors point, for the present at least, to the methods oxidation by chlorine, oxidation by $NaNO_3$ and H_2SO_4, oxidation by HNO_3 and H_2SO_4, and oxidation by $Na_2Cr_2O_7$ utilizing the chrome. The other methods that possess some possibilities are anodic oxidation and oxidation by the atmospheric oxygen in some form, while oxidation by $NaClO_3$ or other chlorate, oxidation by $NaNO_2$, and oxidation by MnO_2 and HCl seem to have a doubtful economic value.

The details of a few methods of preparation of the iron liquor, which have been found suitable, will now be given. They are based on the oxidation by (I) liquid chlorine, (II) sodium nitrate and sulphuric acid, (III) nitric acid and sulphuric acid, and (IV) sodium dichromate. Liquid chlorine, as far as we know, has never been used before. While sodium nitrate and nitric acid used for oxidation in conjunction with sulphuric acid are more or less well known[22] the details of procedure in regard to the proportions of the materials employed, the concentration aimed at and acidity desired, etc., are worked out independently. The condi-

[22] H_2SO_4 and HNO_3 used as early as 1842 by Bordier, and H_2SO_4 and $NaNO_3$ in 1879 by Knapp.

tions as given here are those found capable of producing (1) a high concentration of iron in the liquor, (2) complete oxidation of iron with some excess of the oxidizing agent in the liquor, (3) complete reaction involving the use of a minimum amount of the oxidizing agent and other materials, and (4) a degree of acidity as near that suitable for tanning operation as possible, consistent with the stability of the liquor. *The one difficulty with the prepared sulphate liquor is that, unless the degree of acidity is above a certain minimum it does not keep well and ferric oxide is liable to separate out.* The separation of much ferric oxide would greatly impair the tan liquor and this danger should always be guarded against when the liquor is to be placed on the market where its keeping quality is of vital importance.

(1) *Oxidation by Chlorine.*—For laboratory preparation. A desired weight of commercial copperas is placed in 1¼ to 1½ times its weight of water in a large container provided with an entrance and an exit hole. Through one hole is passed a delivery tube reaching to the bottom of the container. During the passage of the gas, the contents are stirred constantly. As the copperas crystals gradually disappear more can be added until the total weight of the copperas used is equal to the weight of the water present. Toward the end, the exit hole is stopped temporarily to create a small pressure of the chlorine gas above the solution. The completion of oxidation is tested with $K_3Fe(CN)_6$ solution. The end-point should be so permanent that a test sample with $K_3Fe(CN)_6$ solution should be colored deep red and remain so for at least one-half hour in contact with air.

To the liquor 35 per cent. commercial NaCl and 10 per cent. soda ash of the weight of the copperas taken are added, the latter being first dissolved in a small quantity of water and added very slowly with stirring. This liquor thus neutralized should be used without much delay. To make the liquor keep for a short period, pass in again chlorine gas under a small pressure and immediately stopper the bottle tightly. For long storage, it is safer not to add this quantity of Na_2CO_3 until ready for use. The bottle should be tightly closed so that no chlorine gas can escape. No acid need be added to the ferrous sulphate solution for chlorine oxidation.

For commercial preparation, cast iron or enameled iron tanks may be used. Two or three units sould be connected in series and the gas passed in countercurrently.

The liquor thus prepared is dark red in color, but should be absolutely clear, and should remain so without depositing yellow hydrated ferric oxide on standing. It is rather thick and, after the addition of NaCl, has a specific gravity of 1.39. It contains approximately 32 per cent. of iron calculated as $Fe_2(SO_4)_3$.

On the basis of 100 pounds of the drained pelt, the cost of preparation is estimated as follows:

Copperas.....	14 pounds at 1¢	a pound	$0.14
Liquid chlorine.....	2 pounds at 7¢	a pound	.14
NaCl (crude).....	5 pounds at ½¢	a pound	.02½
Na_2CO_3 (comm.).....	1½ pounds at 1½¢	a pound	.02¼
		Total	$0.32¾

This will give approximately 2¾ gallons of the liquor in a concentrated form, weighing about 31 pounds. For use, dilute to 15—25 gallons for drum tannage. The cost of preparation per gallon of the concentrated liquor is estimated to be about 12 cents, or per pound a little over 1 cent.

(II) *Oxidation by* $NaNO_3$ and H_2SO_4.—For laboratory preparation. Take a desired quantity of commercial copperas and place it in a large container containing about 1½ times its weight of water to which have been added 30 per cent. of 66 Bé. H_2SO_4 and 12½ per cent. of Chile saltpetre of the weight of the copperas taken. Heat to boiling and boil gently until brown fumes of NO_2 are finally given off. Remove the burner during evolution of the gas.

Add 20 per cent. NaCl and neutralize slowly with 9½ per cent. soda ash previously dissolved in a small quantity of water. The liquor is ready for immediate use.

For Commercial Preparation. Use an enameled open kettle provided with a steam jacket taking exhaust steam. The kettle should have a somewhat larger capacity, as during evolution of the gas the liquor foams badly.

The evolution of NO_2 fumes indicates the end-point for the reaction and that a small excess of HNO_3 is present. This rep-

resents, of course, a loss in HNO_3 though small, which would otherwise be available for oxidation. But as a small excess is always necessary to carry the reaction to completion, this minor loss seems to be unavoidable.

The above proportion of $NaNO_2$ and H_2SO_4 represents an excess of 15—20 per cent. over the theoretical quantity in each. This is found to be the minimum quantity, especially in the case of $NaNO_2$, in order to secure a complete oxidation without rendering the resulting liquor too alkaline. Rather prolonged boiling is needed before NO_2 fumes are given off, as a certain concentration of HNO_3 in solution must be attained before the complete reaction can take place. But the liquor obtained is more concentrated due to the loss of water by boiling.

Before the addition of NaCl and Na_2CO_3 the liquor has a specific gravity of about 1.50 containing, in this condition, about 30 per cent. $Fe_2(SO_4)_3$. It is a thick liquid, dark red in color. It is absolutely clear and should remain so on long standing without deposition of ferric oxide.

On the basis of 100 pounds, the cost of manufacture is estimated as follows:

Copperas	14 pounds at 1¢	a pound	$0.14
H_2SO_4 (66° Bé.)	4⅛ pounds at 1¢	a pound	.04⅛
Chile Saltpetre	1¾ pounds at 3¢	a pound	.05¼
NaCl	3 pounds at ½¢	a pound	.01½
Soda ash	1½ pounds at 1½¢	a pound	.02¼
		Total	$0.27⅛

This gives approximately 2.5 gallons of the concentrated liquor weighing about 30 pounds before neutralization with soda ash. For use, dilute the liquor to 15—25 gallons for drum tannage. The cost of preparation is estimated to be about 11 cents per gallon of concentrated liquor, or about 1 cent per pound.

(III) *Oxidation by HNO_3 and H_2SO_4.*- For Laboratory Preparation. Take a desired quantity of copperas and place it in a container containing 1½ times its weight of water to which have been added 9½ 10 per cent. of 1.42 HNO_3 and 19 per cent. of 66° Bé. H_2SO_4. Proceed as in (II). 35 per cent. NaCl of the weight of the copperas taken and 9½ per cent. soda ash are later added.

The use of HNO_3 alone without sulphuric acid is very expensive and wasteful.

The liquor has the same general properties as that prepared by (II).

On the basis of 100 pounds of the hide, the cost of manufacture is as follows:

Copperas	14 pounds at 1¢	a pound	$0.14
HNO_3 (1.42)	1⅓ pounds at 8¢	a pound	.20⅔
H_2SO_4 (66° Bé.)	2⅔ pounds at 1¢	a pound	.02⅔
NaCl	5 pounds at ½¢	a pound	.02½
Na_2CO_3	1⅓ pounds at 1½¢	a pound	.02
		Total	$0.31⅚

The resulting liquor is of about the same volume as that in (II) but weighs a little less. The cost of preparation is estimated to be about 13 cents per gallon of concentrated liquor, or a little over 1 cent per pound.

(IV) *Chrome-Iron Liquor.*—For Laboratory Preparation. Take a desired quantity of copperas and place it in an equal weight of water. Add 35 per cent. of 66° Bé. H_2SO_4. Stir until as much of the copperas is dissolved as possible. Cool and add gradually, with stirring and cooling, 20 per cent. of sodium dichromate crystals of the weight of the copperas taken, and then add 30 per cent. NaCl. The liquor is ready for use without neutralization, or with but a small quantity of an alkali added.

For Commercial Preparation. The proportions and procedure hold good, except that an enameled tank or crockery should be used and cooling coils of hard lead should be provided.

Considerable heat is evolved upon the addition of H_2SO_4 and in the introduction of $Na_2Cr_2O_7.2H_2O$, so that cooling facilities should be provided in commercial work when a concentrated liquor is desired. When the liquor is made by the tanners themselves for immediate use, the following procedure can be adopted: For each 100 pounds of the drained skins, take 10 pounds of copperas in 40 pounds or 5 gallons of water, contained in crockery ware. Add 3⅕ pounds of 66° Bé. H_2SO_4, stir well and cool, and then gradually introduce 2 pounds of $Na_2Cr_2O_7.2H_2O$ with good stirring. Dilute to 15—25 gallons for drum tannage. No alkali need be added.

The liquor is rather thick and appears black, as the red color of the iron and the green of the chromic salt tend to neutralize each other. After the addition of NaCl, it has a specific gravity of 1.49 and contains about 26 per cent. iron calculated as $Fe_2(SO_4)_3$ and 8½ per cent. chromium as $Cr_2(SO_4)_3$.

On the basis of 100 pounds of drained pickled sheepskins, the cost of preparation is estimated as follows:

Copperas	10	pounds at	1¢ a pound	$0.10
H_2SO_4 (66° Bé.)	3⅕	pounds at	1¢ a pound	.03⅕
$Na_2Cr_2O_7.2H_2O$	2	pounds at	28¢ a pound	.56
NaCl	3	pounds at	½¢ a pound	.01½
			Total	$0.70⅒

The liquor obtained in this concentrated form measures approximately 2.2 gallons and weighs 27½ pounds. The cost of preparation is about 32 cents a gallon, or 2.6 cents a pound.

This liquor is different from any of the above in that it contains a basic chromic salt as well as ferric salt, which chromic salt also contributes to the tannage. While it costs two and a half times as much as the liquor obtained by any of the first three methods, its cost is still very much less than that of a one-bath chrome liquor.

Section IV. Hydrolysis and Decomposition of Ferric and Chromic Salts Compared.

It may well be suspected that one of the reasons why iron liquor is so much more difficult to manage than chrome liquor might be found in the greater tendency of the ferric salts, particularly the sulphate, in solution to yield readily a precipitate. On the other hand, it may be appreciated why chrome liquor is advantageous when the peculiar properties of the chromic salts are recalled. Chromic salts, both the sulphate and the chloride, in solution are capable of forming "complexes." The bluish hexahydrate chromic chloride, $CrCl_3.6H_2O$, obtained from crystallization in the cold, gives a violet solution which turns green on boiling. This saturated violet solution, when treated with hydrogen chloride gas in the heat yields green crystals, the aqueous solution of which, when freshly prepared, possesses only two chlorine atoms out of the three in the molecule that are precipitable by $AgNO_3$.[23] Chromic sulphate in solution also forms "complexes." The reddish-violet crystals, $Cr_2(SO_4)_3.15H_2O$, gives a bluish violet solution in cold water which also turns green on boiling. This green compound can yield, with H_2SO_4 on warming, products whose SO_4^{-2} radical is not precipitable by $BaCl_2$.[24] The chemistry of chromic salts in solution is certainly a complex one. Certain irregularities in the behavior of a chrome liquor may possibly be due to this complex nature. As far as is known, no such peculiarities exist in the ferric salt solution.

A qualitative comparison between the behavior of a neutral ferric salt solution and a neutral chromic salt solution both in an excessively diluted form is instructive. 1 cc. of a 10 per cent. neutral ferric sulphate solution is diluted to 100 cc. and allowed to stand for 24—36 hours. A fine precipitate of yellow hydrated ferric oxide copiously settles at the bottom. With further dilution to 300 cc. and standing, about two-thirds of the original amount of iron in solution separates out and the solution becomes so depleted that it appears almost colorless. When diluted to 1,000 cc. and allowed to stand for three to four weeks, the solution gives only a slight blue coloration with $K_4Fe(CN)_6$. If a

[23] See Ostwald, "Principles of Inorganic Chemistry," translated by A. Findlay, p. 636 (1914).

[24] *Ibid.* Also Holleman, "A Text Book of Inorganic Chemistry," translated by H. C. Cooper, p. 461 (1916).

normal chromic sulphate is dissolved and diluted to the same degree, only a slight turbidity is observed, but very little, if any, precipitate separates out after 24 hours' standing and the solution remains light green. This comparison shows in a qualitative way that the chromic salt in solution is very much less susceptible of hydrolysis and decomposition with dilution.

Next, a mixture of a basic ferric sulphate and basic chromic sulphate solution was quantitatively studied. This solution is prepared by placing 50 g. of ferrous sulphate crystals in 50 cc. of distilled water containing 17.4 g. C. P., 1.84 H_2SO_4 and then gradually introducing 9 g. of sodium dichromate crystals, $Na_2Cr_2O_7.2H_2O$ to the mixture. Upon introduction of the sodium dichromate, ferrous sulphate crystals are dissolved, much heat is given off, and a thick dark liquid containing a mixture of the basic ferric sulphate and chromic sulphate in solution is obtained. This solution appears black by reflected light and dark red by transmitted light. It has a specific gravity of 1.46. Analysis shows that it contains, per 10 cc.—

0.07312 equivalents of $SO_4^{=}$ (from acidity determination).
0.06820 equivalents of Fe^{+++}.
0.02117 equivalents of Cr^{+++}.

The ratio of the number of equivalents of the sulphate radical $SO_4^{=}$ (which is divalent) to that of Fe and Cr combined (each of which is trivalent) is 0.819 : 1.000, so that there are not enough sulphate radicals to go with iron and chromium in the solution. This condition may be summarized in the formula:

Radical..... M^{III} : $SO_4^{=}$: (OH^-) ($M^{III} = Fe^{+++} + Cr^{+++}$)
Ratio of equiv. 1.000: 0.819 : 0.181 (by difference).

The idea of using such a quantity of H_2SO_4 and making a liquor as concentrated as this needs some explanation. In the first place, if a liquor is to be placed on the market it has to be in as concentrated a form as practicable in order to save freight charge in transportation and to avoid inconvenience in handling. In the second place, a tanning liquor must always contain some degree of basicity. Too much acid left in the liquor not only means just so much alkali needed for neutralization before the tanning operation, but also involves a danger of not getting the proper degree of basicity for tanning in the hands of men who are not quite

familiar with chemistry. We find by a number of experiments that this proportion of the sulphuric acid represents the minimum quantity that should be present in order to make the liquor alkaline enough to be used for tanning without neutralization (Chrome-Iron Joint Tannage) and yet acid enough to make the liquor keep for a considerable period without danger of precipitation.

A quantity of this concentrated liquor measured through a burette is diluted to different volumes with distilled water, and the solution allowed to stand for 24—48 hours. The supernatant liquid is filtered and pipetted for analysis. Chromium is determined by Na_2O_2 oxidation and by titration against sodium thiosulphate solution using KI and starch as indicator. Ferric hydroxide that is precipitated by Na_2O_2 in the same sample is filtered off,* washed and dissolved from the filter with hot dilute HCl solution. The amount of iron in this solution is determined by the Zimmermann-Reinhardt method. These results are tabulated as follows:

* When much iron is present, a considerable amount of the chromate is absorbed by the ferric hydroxide precipitated from the peroxide oxidation, so that the result of the chromium determination in the filtrate is always too low while the iron by the Zimmermann-Reinhardt method becomes high. To avoid this error, the supernatant chromate solution after the peroxide oxidation is decanted through a filter and the ferric hydroxide left in the beaker is dissolved by adding a small amount of hot dilute HCl. The solution is now diluted and the ferric hydroxide re-precipitated with an alkali at a boiling temperature. A small amount of Na_2O_2 may be introduced with the alkali, in which case care must be taken to decompose all the peroxide again. If a large quantity of chromium is also present, a second re-precipitation is necessary in order to remove all the chromium from the ferric hydroxide.

HYDROLYSIS AND DECOMPOSITION OF A MIXTURE OF FERRIC SULPHATE AND CHROMIC SULPHATE IN SOLUTION COMPARED.

Sample	No. of times of dilution	Color of solution after dilution	Character of solution after 3 days standing	Cc. supernatant solution taken for analysis	Cc. $KMnO_4$ sol. consumed N = 0.1139 (for iron)	Cc. $Na_2S_2O_3$ consumed N = 0.04843 (for Cr)	Mg. $Fe_2(SO_4)_3$ in sol. as Fe_2O_3 corr. to 0.2 cc. orig. sol	Mg. $Cr_2(SO_4)_3$ in sol. as Cr_2O_3 corr. to 0.2 cc. orig. sol.	Ratio of Fe_2O_3 to Cr_2O_3 in solution
Orig. conc. solution	No dilution	(Original solution black)	Remains as clear, black solution	10 cc. conc. liquid dilu. to 100 cc. and immediately 5 cc. taken)	9.98	21.87	36.4	10.7	3.40
10 cc. conc. solution dil. to 100 cc.	10	Solution black by refl. light, dark red by trans. light	Black solution, but ppt. at bottom not-iceable	5 (Corr. to ½ cc. orig. sol.)	9.83	21.85	35.8	10.7	3.34
5 cc. conc. solution dil. to 250 cc.	50	Solution dark red. Turbidity after 30 min.	Dark red supernatant solution with yellow ppt. at bottom	10 (Corr. to 0.2 cc. orig. sol.)	3.84	8.71	34.9	10.7	3.26
2 cc. conc. solution dil. to 500 cc.	250	Solution brown Turbidity after 5 min.	Greenish-brown supernatant solution with yellow ppt. at bottom	50 (Corr. to 0.2 cc. orig. sol.)	2.88	8.66	26.2	10.6	2.47
1 cc. conc. solution dil. to 1000 cc.	1000	Solution dull yellow. Turbidity after 3-4 min.	Light green supernatant solution with much yellow ppt. at bottom	200 (Corr. to 0.2 cc. orig. sol.)	1.69	8.55	18.4	10.5	1.47

It is evident that the extent of hydrolysis increases with dilution.

$$\begin{array}{ccc} Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+++} & + & 3SO_4^{=} \\ + & & + \\ 6H_2O \rightleftharpoons 6OH & + & 6H^{+} \\ \Updownarrow & & \Updownarrow \\ 2Fe(OH)_3 & & 3H_2SO_4 \\ \Updownarrow & & \end{array}$$

$Fe_2O_3.xH_2O$ (yellow crystalline ppt. of dehydrated ferric hydroxide).

This is strictly according to the Mass Action principle, for a greater dilution means a greater active mass of water and hence the following reaction is pushed to the right:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + 3H_2SO_4.$$

Another way of interpreting this is that with greater dilution the hydrogen ion concentration is correspondingly lowered. That is to say, the alkalinity of the solution is increased and consequently the degree of hydrolysis is increased.

The above results show how ferric sulphate in solution is more readily hydrolyzed and decomposed than the chromic sulphate. To show this more clearly the following curves are plotted:

Fig. – 1

Curves Showing $Fe_2(SO_4)_3$ and $Cr_2(SO_4)_3$ Remaining in Solution vs. Dilution

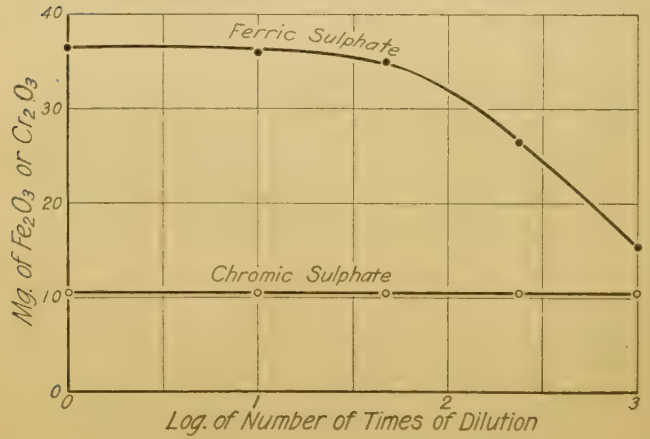
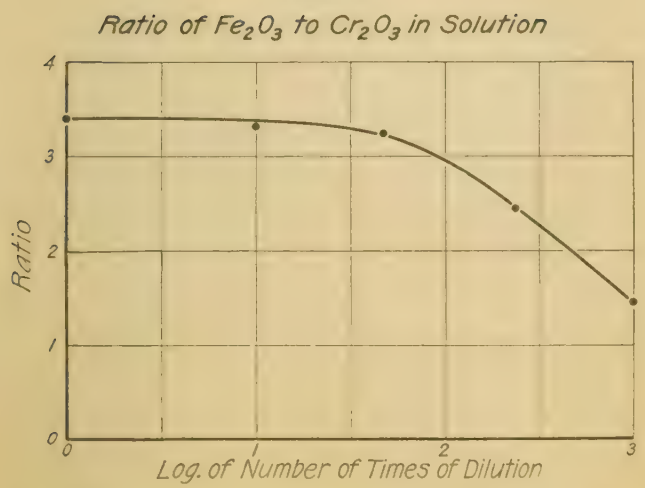


FIG.—II



The precision of the above determinations is not better than ½—1 per cent. For, when the precipitate, especially in the last two solutions, separates out abundantly in a fluffy manner and only the supernatant clear liquid is taken for analysis, the original volume ratio does not exactly hold, but the error is small and can be neglected.

A mixture of the corresponding chlorides, namely the ferric chloride and the chromic chloride, was taken and similarly studied. The basicity relation as determined by analysis was as follows:

Radical..... M^{III} : Cl^- : OH^- ($M^{III} = Fe^{+++} + Cr^{+++}$)

Ratio of equiv. 1.100: 0.800 : 0.200 (by difference).

Dilution in much the same way as in the corresponding sulphate mixture was carried out. In no case was there any precipitate observed, not even where the original solution of the mixture was diluted to 2,000 times, the original solution having a concentration of 34.52 g. iron as Fe_2O_3 and 20.00 g. chromium as Cr_2O_3 per liter. This shows remarkably that ferric chloride is far more stable toward dilution than is ferric sulphate for the same basicity, and in this respect ferric chloride behaves in much the

same way as chromic chloride or other chromic salts. The conclusion to be drawn from this would be that in order to get a stable liquor as much of the ferric salt in the tan liquor as possible should be in the form of a chloride, but unfortunately the main supply of ferrous salt is already in the form of a sulphate ("copperas") owing to the cheapness and convenience of sulphuric acid for pickling purposes in the foundry and steel works. With the chlorine oxidation, however, a third of the acid radical is conveniently secured in the form of a chloride.

Section V. On the Relation of Basicity to Stability in Iron Liquor.

The instability of an iron liquor, or rather, the ease with which hydrated ferric oxide separates out from a solution, depends upon the degree of acidity of the solution. The liquor used in tanning is normally more alkaline than that which corresponds to a neutral salt, *e. g.*, $Fe_2(SO_4)_3$. The liquor, however, reacts acid even when it is constitutionally basic. If an alkali is introduced, the OH^- ions from the alkali tend to precipitate ferric iron as ferric hydroxide or as some basic ferric compound, but the supernatant solution still reacts acid. Only after all the ferric iron has been precipitated, does the solution begin to react alkaline.

It is evident that in order to study the stability of an iron liquor with regard to its basicity, it is necessary to know quantitatively the relation between the Fe^{+++} ion in solution and the acid radical or radicals present. The subject presents some difficulty, as the acid radical in ferric sulphate solution may be composed of, besides the sulphate ion $SO_4^=$, such other negative ions as NO_3^-, Cl^-, etc. This is not uncommon as the ferric sulphate in commerce is generally obtained by the oxidation of copperas with HNO_3 and H_2SO_4, some of the HNO_3 may remain in the ferric salt solution formed. In order to eliminate as much as possible complexities of this nature, there was chosen as the starting point a white powder of ferric sulphate as nearly chemically pure as possible. A solution of this salt (which dissolves very slowly in water) was made containing 133 g. of the air-dried powder to a liter. The solution was allowed to stand in a closed bottle for four weeks, when a small amount of precipitate collected at the bottom. The solution tested for Cl^- with $AgNO_3$ solution gave a negative result. It was then tested for NO_3^- by adding concentrated H_2SO_4 and then ferrous ammonium sulphate solution. No colored ring was observed. This test is not very delicate. With diphenylamine in H_2SO_4 solution a violet to blue coloration is observed, but as the solution contains ferric iron this test for NO_3^- in the presence of iron can not be regarded as conclusive.[25] The test was therefore further elaborated by distilling with ferrous sulphate and H_2SO_4 and receiving the distillate with a 50 cc. 3 per cent. NaOH solution contained in a 250

[25] See Tradwell-Hall, Analytical Chemistry, Vol I, p. 394 (1916).

cc. Erlenmeyer flask. The distillate was acidified and shaken with 5 cc. of chloroform after adding 5 cc. of 10 per cent. KI solution.[26] The test gave a negative result for NO_3. After obtaining conclusive negative tests both for Cl^- and NO_3^-, it was then necessary to determine the quantitative relationships between the ferric iron and the sulphate radical in the solution. For this purpose a 50 cc. portion of this ferric sulphate solution was diluted to 500 cc., 25 cc. of which were taken for each of the analyses described. In order to establish the quantitative relationships accurately it was considered advisable to determine the iron and the acid radical ($SO_4^=$) each by two independent methods. Iron was determined gravimetrically by precipitating with NH_4OH in the presence of NH_4Cl, and independently again by the Zimmermann-Reinhardt volumetric method. The $SO_4^=$ radical was determined gravimetrically by precipitating with $BaCl_2$ in HCl solution and independently again by the acidity determination by titrating in the heat against N/10 NaOH, using 1 cc. ½ per cent. phenolphthalein solution as an indicator. In each analysis at least two portions were carried and the results checked. The results were tabulated as follows:

TABLE II.—Results of Analyses for Fe+++ and $SO_4^=$ by Independent Methods.

	Method of determination	No. of equivalents contained in the 25 cc. (dil. solution)
Fe+++	Zimmermann-Reinhardt	0.003853
	Gravimetric as Fe_2O_3	0.003866
$SO_4^=$	Gravimetric as $BaSO_4$	0.003861
	Titration against N/10 NaOH	0.003872

Note. 1.—The Zimmermann-Reinhardt method is not suited for H_2SO_4 solution because (1) the ferric sulphate solution in the presence of H_2SO_4 has a less pronounced yellow color to guide the reduction by $SnCl_2$, (2) the reduction by $SnCl_2$ is much slower in the H_2SO_4 solution than in the HCl solution, and (3) in the H_2SO_4 solution a precipitate is more liable to form in the solution during the reduction unless a large excess of the H_2SO_4 is present. H_3PO_4 alone without $MnSO_4$ and H_2SO_4 was used. The result was found to be slightly affected by the amount of excess of $SnCl_2$ employed.

Note 2.—In the acid determination by titration with NaOH, the difference between the end points in the cold and in the heat is not great, being about 1 per cent. of the total burette reading in the case of ferric sulphate solution and 1½ to 2 per cent. in the case of ferric chloride solution. It is remarkable to note that the corresponding difference

[26] See A. A. Noyes, Quantitative Chemical Analysis, (1915) p. 113.

in the case of chromic chloride solution is as much as 10 per cent. of the total burette reading.

By "No. of Equivalents" is meant the number of equivalent weights of Fe^{+++} and $SO_4^{=}$ contained in the above 25 cc. of diluted ferric sulphate solution, so that if the solid ferric sulphate from which the solution was made is chemically pure, *i. e.*, contains nothing but $Fe_2(SO_4)_3$ and water, the number of equivalent weights of Fe^{+++} (which represents 3 equivalents per formal weight) should be exactly equal to that of SO_4 (which represents 2 equivalents per formal weight). The ratios of the number of equivalent weights of Fe^{+++} and SO_4 in the solution as determined are as follows:

TABLE III.—Ratios of Equivalents of Fe^{+++} to Equivalents of $SO_4^{=}$ in Ferric Sulphate Solution.

	$SO_4^{=}$ by gravimetric	$SO_4^{=}$ by titration
Fe+++ by Zimmermann-Reinhardt	1.000 : 1.002	1.000 : 1.005
Fe+++ by Gravimetric	1.000 : 0.998	1.000 : 1.002

The closeness with which the above results agree indicates that the ferric sulphate employed is substantially chemically pure. Knowing the exact constitution of the ferric salt solution it was then necessary to study the stability of the ferric salt in solution by changing the degree of basicity. This was done by adding a calculated amount of Na_2CO_3 solution of a known strength to a given quantity of $Fe_2(SO_4)_3$ solution and finally making up to the same total volume with distilled water in each case. In this study there was employed a strength of the ferric salt solution in each case not far from that of the iron liquor used in the actual drum tanning operation. This was estimated to be from 2 to 4 per cent. iron calculated as $Fe_2(SO_4)_3$. In this connection it might be added that Na_2CO_3 was used rather than NaOH, as in actual practice in the tannery sal soda or sodium bicarbonate is generally used for such a purpose. A 0.5000 N Na_2CO_3 solution was made from a thoroughly dried, anhydrous C. P. sodium carbonate. For study, a 25 cc. portion of the above ferric sulphate solution containing 10.20 g. $Fe_2(SO_4)_3$ per 100 cc. was taken, a calculated quantity of this Na_2CO_3 solution run in from a burette, and the total volume made up to 65 cc. with distilled water. The results were tabulated in Table IV. Although during the introduction of

Na_2CO_3 there was a brisk evolution of CO_2 gas, there remained in the suspension some $CO_3^=$ ions in addition to the OH^- ions, so that the precipitate formed was in the nature of a basic ferric carbonate or a mixture of ferric hydroxide and ferric carbonate.* It was noted that the precipitate separated out from No. 7 more readily than it did from Nos. 8, 9, 10, and 11. It is clear that the ferric sulphate solution having a basicity higher than that which corresponds to No. 6 is unstable and a yellow precipitate of $Fe_2O_3.xH_2O$ or some basic ferric carbonate soon separates out. It was found from the tanning experiments also that this degree of basicity in the case of a sulphate liquor was as high as could safely be employed without danger of causing a yellow precipitate to separate out on short standing and also that if the iron liquor employed was of a higher basicity than this, it would rapidly impart a yellow color to the surface of the pelt after drumming from 15 to 30 minutes.

Because of the purely scientific interest involved NaOH was also used in place of Na_2CO_3 so that in this case only OH^- ions were introduced and the complication of having some $CO_3^=$ ions present in the solutions was eliminated. The results are shown in Table V. Comparing Table IV and Table V, it is remarkable to note how the two series run parallel to each other. Table V like Table IV also indicates that in the case of the sulphate liquor Nos. 6 and 7 represent the highest basicity beyond which the iron liquor yields much precipitate. The difference between the two series is that in the case of Na_2CO_3 any precipitate first formed can be caused to disappear on continued shaking to a thick solution from which the final precipitate appears after a lapse of from 12 to 30 minutes thereafter while the precipitate from the NaOH solutions is immediate and persistent. The color of the solutions in Table V is also somewhat deeper. The report that the best iron liquor to be employed for tanning is that which possesses a basicity corresponding to the formula $Fe(OH)SO_4$ is not borne out by this study or by the tanning experiments.

There are other evidences that independently show that

* To determine how much $CO_3^=$ is present in the suspension, CO_2 was distilled from it after the precipitate had just separated out, with excess of H_2SO_4 and received in a known NaOH solution. Titration gave the amount of $CO_3^=$ present in the suspension to be 63.6 per cent. of the total added.

$Fe(OH)SO_4$, or a basic ferric sulphate corresponding to this basicity, is very unstable and rapidly yields a precipitate from its solution. For instance, when a ferrous sulphate solution is oxidized by hydrogen peroxide without the addition of any acid, a precipitate is soon formed in the solution. This basic ferric sulphate is formed by the following reaction:

$$2FeSO_4 + H_2O_2 \longrightarrow 2Fe(OH)SO_4.$$

Other neutral oxidizing agents, such as $KBrO_3$, that can effect this oxidation without the addition of an acid to the neutral ferrous sulphate solution, produce similar precipitates in the resulting ferric salt solution.

In the case of ferric chloride solution, the difference is astonishing. A similar series of the ferric chloride solution was studied using Na_2CO_3 solution. The results are tabulated in Table VI. It is remarkable that throughout the whole series studied no precipitate was formed after one week's standing even where the basicity ratio was higher than the highest in the sulphate series studied above. This shows indeed that the ferric chloride is far more stable in a basic solution than the corresponding sulphate. After two weeks' standing, however, precipitate began to appear in solutions Nos. 3, 4, 5, and 6. It is interesting to note that here as in the sulphate series above (Tables IV and V) the precipitate separated out more readily from solutions of lower basicity in the series (Nos. 3, 4, 5, and 6) than form those at the end having high basicities, such as Nos. 10, 11, or 12.

The "acidity" determination, according to the method of Thomas and Baldwin[27] for the solutions of various basicity in the series studied above, can not be made in the case of the ferric salt solution, because it is found that ferric iron is rapidly reduced by the hydrogen in the presence of the platinum electrode, and no reading can be obtained.

The determination of the hydrogen ion concentration ("acidity") in iron tan liquor by a study of the rate of hydrolysis of sucrose has also a similar difficulty as one of the products of hydrolysis (glucose) has a reducing action on the ferric iron in the hot solution.

[27] "The Acidity of Chrome Liquors," by A. W. Thomas and M. E. Baldwin, This Jour., May, 1918, p. 192.

TABLE IV. 25 cc. Solution Containing 10.26 g. $Fe_2(SO_4)_3$ per 100 cc. with Addition of a Calculated Amount of N/2 Na_2CO_3 Solution and Dilution to a Total Volume of 65 cc.

No.	Cc. Na_2CO_3 added N = 0.5000	Cc. water added to make up 65 cc.	Basicity ratio $\frac{\text{Equiv. } Fe^{+++}}{\text{Equiv. } SO_4^{=}}$	Color of sol. obtained	Time ppt. begins to form after adding Na_2CO_3	Appearance overnight (18 hours)
1	0.00	40.00	1	Straw yellow	———	Clear solution
2	2.66	37.34	29/28	Yellow	———	Clear solution
3	5.14	34.86	15/14	Red-yellow	———	Clear solution
4	8.57	31.43	9/8	Red	———	Clear solution
5	11.02	28.98	7/6	Bright red	———	Clear solution
6	12.86	27.14	6/5	Bright red	Turbidity first noticed after 50 min.	Bright red sol. with some yellow ppt.
7	15.43	24.57	5/4	Deep red	Ppt. after 12-15 min.	Bright red sol. with more yellow ppt.
8	19.29	20.71	4/3	Deep red	Ppt. after 15-20 min.	Bright red sol. with more yellow ppt.
9	25.71	14.29	3/2	Dark red	Ppt. after 25-30 min.	Red sol. with much yellow ppt.
10	30.86	9.14	5/3	Very dark red	Ppt. after 25-30 min.	Reddish-yellow super. sol. with yellow ppt. (1/5 of total vol.)
11	38.57	1.43	2	Black-red	Ppt. formed after addition, disappears on shaking. Ppt. after 25 min.	Yellow super. sol. with yellow ppt. (3/4 of total vol.)
12	46.30	——*	5/2	Black-red	Ppt. formed after addition, disappears on prolonged shaking. Ppt. after 20 min.	Light yellow super. sol. with yellow ppt. (4/5 of total vol.)

* The total volume of this solution is 71.30 instead of 65 cc.

TABLE V — 25 cc. Solution Containing 10.26 g. $Fe_2(SO_4)_3$ per 100 cc. with Addition of a Calculated Amount of NaOH Solution and Dilution to a Total Volume of 65 cc.

No.	Cc. NaOH added N / 0.4923 Trd. M. O. N / 0.4850 Trd. Phenolphthalein	Cc. H_2O added to make 65 cc.	Basicity ratio Equiv. Fe^{+++} / Equiv. $SO_4^{=}$	Color of solution after addition NaOH	Appearance after 30 hours' standing
1	0.00	40.00	1	(Straw yellow from start)	Straw yellow solution
2	2.70	37.30	29/28	Yellow	Reddish yellow solution
3	5.22	34.78	15/14	Reddish yellow	Light wine red solution
4	8.70	31.30	9/8	Red	Red solution
5	11.11	28.82	7/6	Deep red	Deep red solution
6	13.04	26.96	6/5	Deep red cloudy sol.	Deep red solution (Slightly turbid)
7	15.66	24.34	5/4	Deep red cloudy sol.	Deep red turbid sol. with some yellow ppt.
8	19.56	20.44	4/3	Deep red turbid sol.	Deep red turbid sol. with yellow ppt.
9	26.09	13.91	3/2	Dark red suspension	Yellow-red turbid sol. with yellow ppt. 1/6 of total volume
10	31.30	8.70	5/3	Dark red suspension	Yellow-red turbid sol. with yellow ppt. 1/5 of total volume
11	39.11	0.89	2	Black red suspension	Yellow clear super. sol. with yellow ppt 1/3 of total volume
12	47.00	- *	5/2	Black red suspension	Straw yellow clear super. sol. with yellow ppt. 1/2 of total volume

* The total volume of this solution is 71.30 instead of 65 cc.

TABLE VI.—25 cc. Ferric Chloride Solution Containing 0.03228 Equiv. Fe^{+++} and 0.03042 Equiv. Cl^{-} with Addition of a Calculated Amount of N/2 Na_2CO_3, and Dilution to a Total Volume of 65 cc.

No.	Cc. Na_2CO_3 added N = 0.5000	Cc. H_2O added to make 65 cc.	Basicity ratio $\frac{\text{Equiv. } Fe^{+++}}{\text{Equiv. } Cl^{-}}$	Color of solution obtained	Appearance after 2 week's standing	Appearance after 15 week's standing
1	——	40.00	$\frac{.03238}{.03042} = 1.064$	Light yellow	Clear	Clear, no ppt.
2	0.40	39.60	15/14	Yellow	Clear	Ppt. at bottom
3	3.28	36.72	9/8	Reddish yellow	Turbid with ppt. of yellow oxide	Ppt. at bottom
4	5.34	34.66	7/6	Yellow-red	Turbid	Ppt. at bottom
5	6.88	33.12	6/5	Red	Cloudy	Cloudy, no ppt.
6	9.04	30.96	5/4	Red	Cloudy	Cloudy, no ppt.
7	12.28	27.72	4/3	Deep red	Slightly cloudy	Slightly cloudy, no ppt.
8	17.68	22.32	3/2	Dark red	Clear	Clear, no ppt.
9	21.98	18.02	5/3	Dark red	Clear	Clear, no ppt.
10	28.46	11.54	2	Very dark red	Clear	Clear, no ppt.
11	34.96	5.04	5/2	Very dark red	Clear	Clear, no ppt.
12	47.88	——*	5	Black-red	Clear	Clear, no ppt.

* The total volume of this solution is 72.88 cc. instead of 65.00 cc.

Section VI. Behavior of the Pelt Towards Iron Tan Liquor.

In view of the report[28] that iron tan liquor has the same acidity at the end of the tanning operation as it had at the beginning and also of a proposed process of iron tannage[29] using the iron tan liquor over and over again in a cycle without mentioning the necessity of readjusting the acidity of the liquor it was thought advisable to study this matter. Pickled sheepskin was cut into rectangular pieces of about 4 inches by 5 inches. These pieces were placed in tepid water for a short time and, when softened, introduced into cold water containing a small amount of salt to prevent plumping. The skin was then carefully neutralized with Na_2CO_3 until all mineral acid was removed, using methyl orange as an indicator. The skin was rinsed off and the excess water squeezed out so that it was roughly in the same condition as pickled skins that have been horsed up over night. The reason for neutralizing the skin in our experiments was to avoid introducing into the tan liquor an indefinite amount of the mineral acid present in the pickled skin. The tan liquor used in these experiments was a basic ferric sulphate or chloride solution, having in general a basicity of 3 equivalents of mineral acid radical to 4 equivalents of Fe^{+++} and containing iron from 11½ to 16½ g. Fe_2O_3 per liter. The volume of the tan liquor in cc. equaled from 3 to 4 times the weight in grams of the skin with excess water pressed out. Tanning was carried out in a glass jar of 1⅛ liters capacity set in a bottle shaker making about 35 R. P. M. The actual weight of the skin in these experiments was from 150 to 200 grams, and the total volume of the tan liquor 600 cc. The amount of iron used (calculated as Fe_2O_3, therefore, varied from 4.0 to 6.0 per cent. of the weight of the pelt in the thoroughly drained condition. Both Na_2CO_3 and NaOH were employed to bring about the proper basicity in the liquor for tanning. In the case of Na_2CO_3, CO_2 gas continued to be given off during tanning.

The detailed procedure was as follows. A desired amount of the stock ferric solution of known concentration and acidity was

[28] "Notes sur le Tannage aux Sels de Fer," by V. Casaburi, *Le Cuir*, August 1, 1919.

[29] Bystron and Vietinghoff's Patent (German Pats. Nos. 255,320 et seq.).

taken, and a calculated quantity of NaOH or Na_2CO_3 solution of known strength added in order to obtain the desired basicity for tanning. The solution was then diluted according to the above volume relation. The skin was immediately placed in the liquor and the container shaken in the bottle shaker. 5 cc. samples were taken for analysis at an interval of 15 minutes or longer. Iron was determined by the Zimmermann-Reinhardt method and the acidity (H_2SO_4 or HCl) by NaOH titration using 1 cc. ½ per cent. phenolphthalein solution as an indicator.* The acid determination was obtained by titration with N/10 NaOH first in the cold; and after the end-point has been reached, the solution was brought to just below boiling and titration continued until the end point was again reached. The difference between the cold and the hot end-points was only 0.15 to 0.35 cc. N/10 NaOH for a total burette reading of 10—30 cc. Four independent experiments were carried out in the case of the ferric sulphate liquor, but one set of data and results from one of these experiments will be given here which may be considered as typical.

FERRIC SULPHATE TAN LIQUOR.

Data:

Sheepskin (with excess water pressed out).....	167 g.
Ferric sulphate liquor—	
(a) Volume for tanning.....	600 cc.
(b) Concentration (calculated as Fe_2O_3)....	16.33 g. per l.
(c) Ratio of $\frac{(SO_4= \text{ Equiv.})}{(Fe+++ \text{ Equiv.})}$	0.742
Salt (about 5½ per cent.).....	9 g.

* Mineral acid and iron can be determined in the same sample by first titrating with NaOH solution in the hot, allowing ferric hydroxide to collect at the bottom, filtering off the precipitate, dissolving it from the filter with a hot, dilute HCl, and then determining the iron in solution by the Zimmermann-Reinhardt method.

The results are tabulated in Table VII. The skin at the end of each experiment was well tanned save for the neutralization operation which would be required in actual practice.

TABLE VII.—Behavior of Neutral Pelt Towards Basic Ferric Sulphate Liquor.

Sample No.	Time interval between which samples were taken	H_2^+ $SO_4^=$ Cc. NaOH in the hot N = 0.1096	H_2^+ $SO_4^=$ Equiv H_2SO_4 per l.	Fe^{+++} Cc. $KMnO_4$ N = 0.1004	Fe^{+++} Equiv iron per l.	Ratio of $SO_4^=$ to Fe^{+++} Equiv.
1*	———	20.72	0.455	10.17	0.613	742 : 1000
2	15 min.	17.88	0.392	8.63	0.520	754 : 1000
3	15 min.	16.80	0.368	7.51	0.452	815 : 1000
4	15 min.	16.13	0.354	7.21	0.435	814 : 1000
5	15 min.	15.86	0.348	6.80	0.410	849 : 1000
6	15 min.	15.54	0.341	6.61	0.398	858: 1000
7	15 min.	15.30	0.336	6.45	0.388	866 : 1000
8	15 min.	15.15	0.332	6.38	0.385	862 : 1000
9	15 min.	15.10	0.331	6.34	0.382	867 : 1000
10	30 min.	14.87	0.326	6.28	0.378	862 : 1000
11	24 hrs. Continuous shaking	14.51	0.318	6.17	0.372	855 : 1000

*Note. The sample of this basic ferric sulphate tan liquor yielded a precipitate on standing, but after the skin was placed in it and tanned, all subsequent samples no longer yielded any precipitate. During tanning, the color of the liquor became lighter—from deep red to yellow—and the skin, on the other hand, was gradually colored red.

An additional experiment was carried out using a ferric chloride liquor in place of the ferric sulphate liquor used above. In the following are tabulated the data of this experiment.

Ferric Chloride Tan Liquor.

Data:

Sheepskin (with excess water pressed out)..... 152 g.

Ferric chloride liquor—

(a) Volume for tanning..... 600 cc.

(b) Concentration (calculated as Fe_2O_3).... 11.60 g. per l.

(c) Ratio of $\frac{\text{(Cl}^-\text{ Equiv.)}}{\text{(Fe}^{+++}\text{ Equiv.)}}$ 0.765

Salt (about 5 per cent.)..... 8 g.

The results are tabulated in Table VIII. As in the case of the experiments using ferric sulphate liquor the skin was also well tanned in the ferric chloride liquor and no neutralization was effected.

TABLE VIII.—Behavior of Neutral Pelt Towards Basic Ferric Chloride Liquor.

Sample No.	Time interval between which samples were taken	HCl		Fe^{+++}		Ratio of Equiv. of Cl^- to Fe^{+++}
		Cc. NaOH in the hot N = 0.1104	Equiv. HCl per l.	Cc. $KMnO_4$ N = 0.1087	Equiv. iron per l.	
1*	———	15.00	0.333	6.66	0.435	765 : 1000
2	15 min.	13.16	0.291	5.74	0.374	778 : 1000
3	15 min.	12.44	0.275	5.31	0.346	795 : 1000
4	15 min.	12.07	0.267	5.07	0.331	806 : 1000
5	15 min.	11.95	0.264	4.76	0.311	849 : 1000
6	15 min.	11.90	0.263	4.63	0.302	871 : 1000
7	15 min.	11.89	0.263	4.59	0.300	876 : 1000
8	15 min.	11.82	0.261	4.61	0.301	868 : 1000
9	15 min.	11.80	0.261	4.51	0.294	887 : 1000
10	24 hrs. Continuous shaking	11.70	0.259	4.47	0.292	887 : 1000

*Note.—None of these samples (including sample No. 1) of this basic ferric chloride liquor yielded any precipitate on standing. The colors of these samples were decreased from deep red (sample No. 1) to light yellow (sample No. 10). On the other hand, the red color of the skins became deepened as the tanning operation progressed.

From these results the following important conclusions can be drawn:

(1) Iron is taken up by the skin very rapidly at the beginning of the tanning operation, and from 30 to 40 per cent. of the total is taken up by the pelt before neutralization.

(2) The mineral acid (sulphuric acid or hydrochloric acid) is also taken up by the skin in a similar manner, the total amount absorbed by the neutral pelt being in general about 20 to 30 per cent. of the total. (If pickled skins are not neutralized before tanning as in actual practice, a correspondingly less amount of the acid will be taken up by the skin. That the skin absorbs the sulphuric or hydrochloric acid from the liquor is corroborated in actual tanning practice by the fact that only 70—80 per cent. of the theoretical amount of alkali is required to effect the complete neutralization. See later Section on Pure Iron Tannage.)

(3) Although the mineral acid is also taken up by the pelt, it is not taken up in the same proportion as the iron so that the liquor is more acid towards the end of the tanning operation than at the beginning.

(4) The curves of absorption of both the iron and the acid by the pelt with respect to the time of tanning approach some constant horizontal lines asymptotically.

(5) The tanning reaction is practically completed within one and a half hours of drumming and the neutralization operation can begin after $1\frac{1}{4}$ to $1\frac{1}{2}$ hours of drumming, it being neither necessary nor advisable to allow the pelt to remain in the liquor for longer than $1\frac{1}{2}$ hours before neutralization takes place.

(6) Both the basic ferric sulphate liquor and the basic ferric chloride liquor behave alike towards the pelt, the only difference being that the ferric chloride liquor possesses decidedly less tendency to yield the precipitate of hydrated ferric oxide than does the ferric sulphate liquor.

Although burette readings for NaOH are expressed in four significant figures, the precision for the results obtained in many cases is probably not much better than 1 per cent. For, in the first place, the samples taken for analysis are small (only 5 cc.) and, in the second place, the organic particles, such as fatty matters, skin fibers, etc., present in the tan liquor make accurate sampling rather difficult. Furthermore, the presence of grease causes tiny drops of the liquor to adhere to the walls of the pipette, so that frequent cleaning by means of a cleaning solution is necessary. Considerable difficulty is also experienced due to the fact that the presence of the organic matter in the liquor interferes with the determination of iron by the $KMnO_4$ titration. This difficulty is finally overcome by oxidizing all the organic matter present in the sample with $KMnO_4$ in the presence of HCl until a purple color is seen. The sample is then heated, reduced with $SnCl_2$, and titrated with $KMnO_4$ solution in the usual manner.

It was observed in tanning experiments using a wooden drum that a completely oxidized iron tan liquor gave a copious precipitate when tested with $K_4Fe(CN)_6$ solution at the end of the tanning operation. Evidently the tan liquor is subject to reduction by the skin, the woody material and the metallic parts of the drum, and organic impurities that may collect in the drum. The amount of reduction in the tan liquor by the skin alone has been determined. For such purpose, the skin was tanned in a glass container with a completely oxidized ferric sulphate liquor. The

FIG. — III

Curves Showing Absorption of Fe and H_2SO_4 during Tanning

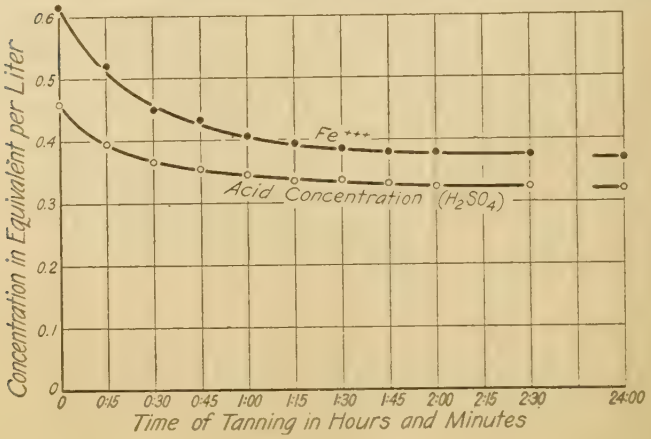


FIG. — IV

Curve Showing Increase in Acid Concentration during Tanning For Ferric Sulphate Liquor

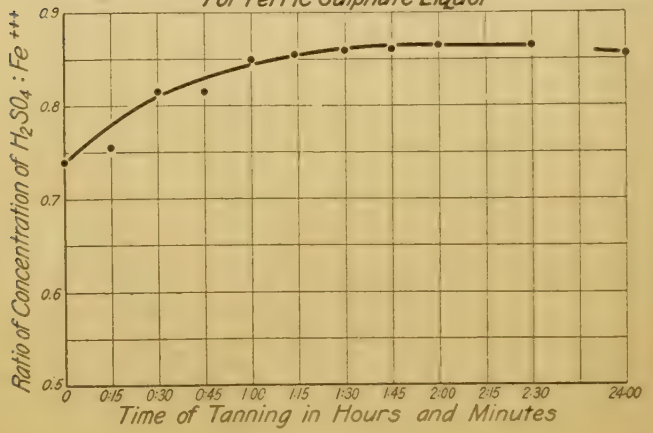


FIG – V

Curves Showing Absorption of Fe and HCl during Tanning

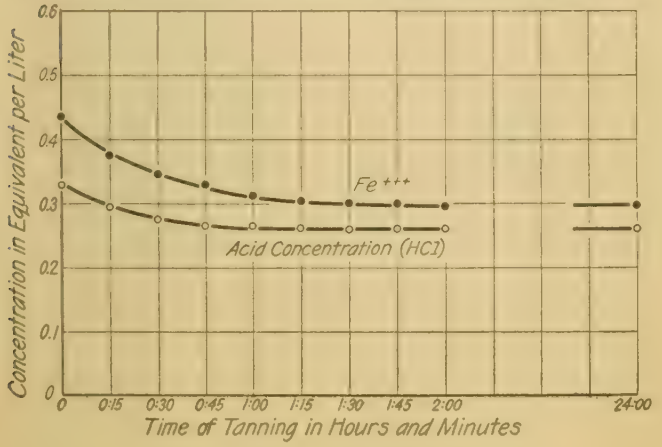
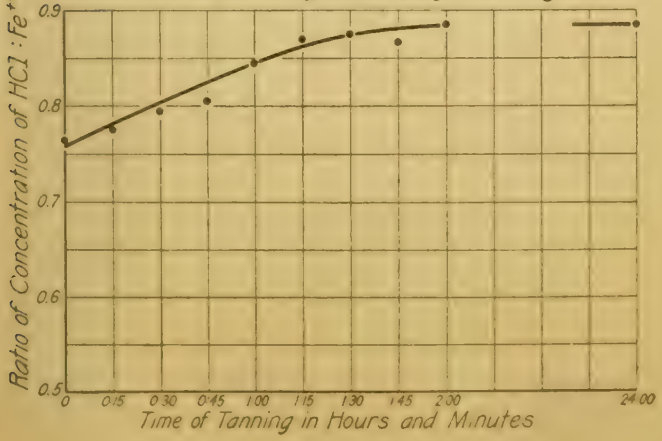


FIG – VI

Curve Showing Increase in Acid Concentration in $FeCl_3$ Tan Liquor during Tanning



skin was allowed to remain in the liquor with continuous shaking for 24 hours. In this particular experiment, an amount of iron containing 14½ per cent. $Fe_2(SO_4)_3$ of the weight of the drained skin, dissolved in water equal to 3½ times the weight of the skin, was used. Ferric iron in the sample taken at the end of 24 hours was determined by means of a titanous sulphate, $Ti_2(SO_4)_3$ in H_2SO_4 solution using ½ cc. normal NH_4CNS solution as an indicator, while total iron was determined by $KMnO_4$ titration after oxidizing off all the organic impurities in the sample with $KMnO_4$. It was found that 4.4 per cent. of the total iron in the liquor had been reduced to the ferrous state. This amount of reduction was exclusively due to the skin. In actual practice where a wooden drum is used with whatever dirt that may collect in it, the percentage of the iron reduced must be greater.

Section VII. Experiments on Tanning With Ferric Hydroxide Hydrosol.

A ferric hydroxide hydrosol was prepared and applied to tanning for two reasons: (1) that it was desired to study the tanning action of ferric iron completely in the colloid state, and (2) that as a sol requires for its stability only the small amount of an electrolyte that is retained with the colloid,* the tan liquor can be considered to be practically free from an electrolyte and consequently the function of a neutral electrolyte such as NaCl, Na_2SO_4, etc., used in a mineral tanning liquor will thereby be disclosed. The sol was made by the peptization method. For such a purpose a fairly concentrated (about 30 per cent.) ferric chloride solution was taken and a dilute ammonia solution (1 vol. 0.90 NH_4OH to 8 or 10 vol. water) added drop by drop, while the solution was stirred by a mechanical stirrer. On adding NH_4OH the yellow red solution turned brown and finally almost black by reflected light. The addition of NH_4 was continued until solid particles of ferric hydroxide were re-dissolved only after 5 to 10 minutes continuous stirring. The sol was dialyzed in collodion sacks first in running tap water over night and then in distilled water for 6 days, changing the distilled water three times every 24 hours. The sol thus obtained was rather diluted as much water had entered the sacks during dialysis by virtue of the osmotic pressure, and it was necessary to concentrate it by evaporation. After concentration it was filtered through cotton.

This sol was coagulated by an electrolyte such as NaCl when a certain concentration of it was reached. On standing the coagulated ferric hydroxide settled at the bottom, leaving the supernatant solution colorless. When it was coagulated by HCl, added in some excess, however, the precipitate, on standing, re-dissolved giving a yellow solution of ferric chloride. A dilute sol prepared as above but dialyzed for seven days showed a misty beam of light under an ultramicroscope. The particles are so small that they can not be counted and their motions are not discernible although a distinct mist is seen. The electrical charge of the sol was determined by cataphoresis. This was determined in the ordinary U-tubes using KCl solution of the same conductivity as the sol in

* The "Complex" Theory of Colloids.

the upper portions of each branch in which the electrode was immersed. The sol moved toward the negative electrode, showing it to be positively charged, as would have been expected.

The tanning action of the sol toward a carefully neutralized, nearly salt-free sheepskin was studied. For this purpose, a piece of pickled sheepskin (4¾ in. x 8¾ in.) was first softened in water in the presence of a small amount of salt. It was carefully neutralized with Na_2CO_3 solution using methyl orange as an indicator, and the salt was washed out from the skin as far as possible (without causing undue plumping) when only a small amount of AgCl was formed in the wash water tested with an $AgNO_3$ solution. The excess water was pressed out from the skin and its weight in this condition was 51 g. A 250 cc. portion of the ferric hydroxide hydrosol (analysis giving 0.963 g. Fe_2O_3 per 100 cc.) was taken and the neutralized, nearly salt-free skin shaken in it continuously for 2½ hours. The sol was not coagulated but the skin swelled to about three times its original thickness, becoming stiff and rubber-like. It was not tanned. Five per cent. salt (2.5 g.) was next added and the shaking continued for one hour longer. The skin had fallen but was not tanned and the inner layer was not even penetrated. The sol was coagulated by the addition of the sodium chloride.

The experiment was repeated in exactly the same manner, using, however, a well pickled skin instead of the de-pickled and salt-free skin. No salt was added. The hydrosol was again coagulated by the small amount of the H_2SO_4 and NaCl left in the pickled skin, yet the skin swelled badly. The cross section of the skin showed red lines on the outside edges and a large white untanned band in between.

From this it appears that the presence of an electrolyte such as NaCl or Na_2SO_4 in the tan liquor is to prevent plumping so that the pelt is kept "fallen" in the liquor so as to be readily penetrated by the tanning agent. It must be observed that the plumping of the pelt in the hydrosol is not caused by the acid liberated during tanning, for there is only a negligible amount of an acid radical that can be retained in the sol, but by simple inhibition of water by the gelatine material of the pelt in this neutral sol. It appears also that ferric hydroxide in a pure sol form can not be employed for tanning purposes; for without a sufficient amount

of an electrolyte, the pelt would be caused to swell and not be penetrated; but if sufficient electrolyte is added to prevent plumping, the sol is coagulated at once to a gel which likewise would not penetrate the pelt. It is evident that a pure iron sol will not act as a tanning agent; hence the theory of leather formation by colloidal co-precipitation alone is open to doubt, and the reaction may be purely chemical.

Section VIII. General Experimental Work on Iron Tanning.

The requirements of a good tannage are (1) that the pelt shall be converted into a net work of isolated fibers and become no longer putrescible, and (2) that this conversion shall be irreversible, *i. e.*, the leather so obtained shall not be readily affected, or reverted to the raw condition, by water or other agency (acid-alkali treatments excepted). In addition it might be mentioned that the leather obtained shall keep well, *i. e.*, it shall not spontaneously deteriorate on storing or in use within a reasonable length of period. Iron tannage can yield a leather that will fulfill all these requirements when it is properly carried out.

In research work on this subject many difficulties have been encountered. Since no detailed data on the subject are available in the existing literature, much time has been spent in determining conditions for a successful working. A ferrous sulphate solution was employed as such and found to have no tanning property.* Oxidation of the iron was then resorted to, but the question arose as to what oxidizing agent should be employed and in what manner the oxidation should be effected. Sodium nitrite and sulphuric acid, bleaching powder and acetic acid or sulphuric acid, sodium dichromate and sulphuric acid were among the oxidizing agents first employed. The question of completeness in oxidation, the relation of acidity of ferrous sulphate solution to oxidation, and the reduction of the ferric iron in the liquor by organic materials in contact with it were matters that were gradually brought to light. The basicity of the iron liquor used for tanning exercised

* The experiment was carried out as follows:

Skin (sheepskin pickled, with water pressed out)	40	g.
Salt (5 per cent.)	2	g.
Ferrous sulphate ($FeSO_4.7H_2O$) (14 per cent.)	5.6	g.
Water (3 times the weight of skin)	120	cc.

The solution was then made slightly alkaline up to the point of the beginning of the precipitation of the green $Fe(OH)_2$. The skin was shaken in it for 1½ hours and found to remain soft and unaffected. On drying the skin so treated was practically in the same condition as a dry pickled skin with dark spots and areas of contracted grain shown on the grain side. It was affected by water and plumped in it.

an unlooked-for influence.** For, when it was not properly adjusted, either no satisfactory tannage was obtained, or much yellow precipitate was deposited so that the pelt was difficult to tan through.

After some experimentation a tannage was found possible and the pelt was apparently well tanned while in wet condition. On drying, however, the pelt shrunk and the color of the grain was uneven. Dark wrinkled spots appeared on the grain and often the skin on drying looked horny and transparent. The leather was stiff, and the grain brittle.†

Since a comparatively high percentage of the iron salt of the weight of the pelt is needed, this necessitates the use of a small amount of water and the employment of a somewhat concentrated liquor ("short liquor") in an attempt to cut down the quantity of

**To investigate the effect of the basicity of the tan liquor on the skin (neutralized) tanned in it, four tan liquors with different degrees of basicity were prepared and the skins tanned in them. The skins, after being shaken in these liquors for 15 minutes, were examined and the results tabulated as follows:

TABLE IX.

Basicity ratio $\frac{\text{Equiv. Fe}^{+++}}{\text{Equiv. SO}_4^{=}}$	Color of tan liquor	Color of skin shaken for 15 min	Character of skin after 15 min shaking
6/5	Deep red (Clear sol.)	Reddish straw color	Skin penetrated by sol.
5/4	Dark red (Clear sol.)	Light red	Skin tanned through
4/3	Dark red (Cloudy sol.)	Red-yellow	Skin tanned through
3/2	Black red Turbid sus.	Brown-yellow	Pigment crust on surface layer Skin barely tanned through

It will be noticed that when the liquor is of the right basicity the color of the skin in contact with it should be more red than yellow.

† If, however, before the pelt (skin) was permitted to dry completely it was stretched or knee-slaked while still in a sammied condition, the brittleness of the grain on complete drying could be overcome. This amounts to separating the fibers by mechanical means rather than from the natural result of tanning. A well pickled skin could be made soft and flexible as if tanned, when worked in the same way.

the iron salt taken.* The phenomenon of "grain drawing" is then apt to occur if the liquor is not carefully introduced and the pelt properly prepared.

Finally, after satisfactory tannage could be obtained the problem of coloring presented another phase of difficulty. The yellow-red color of the leather makes dyeing to a light color ("fancy color") impossible. Further, the iron in the leather is active so that it combines with many substances to form insoluble compounds having generally an objectionable color. Vegetable retanning is limited to cases where a gray or black leather is desired. The interference of iron with dyeing by means of basic dyes to a color other than black constitutes another difficulty on account of the chemical action of iron on many a vegetable mordant required when such dyes are to be used. On the other hand, in certain cases where chemical activity of iron is utilized for the coloring of the leather by a treatment with substances capable of producing color lakes with iron (*e. g.*, with $K_4Fe(CN)_6$ for blue coloring) the leather then becomes hard and brittle, probably due to the withdrawal of iron from the fibers for the formation of the inert color lakes. Consequently the leather is to a greater or less extent detanned.† Furthermore, the color of the leather thus produced is not fast and is slowly washed out unless this treatment is immediately followed by oiling or fat-liquoring. On the other hand, the same detanning effect also results when an attempt is made to bleach the iron tanned leather by means of a reducing agent such as bisulphite or thiosulphate followed by an acid.

Some methods that have been employed to overcome these difficulties may be mentioned. It was found that improper tannage more than anything else was responsible for the brittleness of the leather. When a pelt is not uniformly tanned through, due to either the liquor employed being too alkaline or subsequent neu-

* Similar improvement has been successfully made in chrome tannage. Thus, from a private communication, a process of two-bath chrome tannage for skins consisting of (1) *pickling* with 3 per cent. salt, 1 per cent. 66° Bé. H_2SO_4 in 2 gallons water per 100 pounds, drumming for 20 minutes; (2) *chroming* with 3 per cent. $Na_2Cr_2O_7.2H_2O$, 1 per cent. 66° Bé. H_2SO_4 in 2 gallons water, drumming for 2 hours; and (3) *reducing* with 1½ per cent. 66° Bé. H_2SO_4 in 1 gallon water (added first) and 14½ per cent. "hypo" in 2 gallons of water, drumming for 2 hours, has been successfully employed, giving a very soft, light-colored leather.

† If the neutralized tanned pelt is first dried to "crust" and then wetted back for this treatment, the effect of detanning is less marked.

tralization too rapid, the outer layer (the grain) becomes dense and crusty, while the inner layer remains soft. The whole pelt on drying, therefore does not contract uniformly and the shrinking or curling up of the pelt results. This leads to the breaking of the grain on bending. When much iron in the tan liquor has been reduced to the ferrous state and found its way to the pelt, it will become oxidized during drying. This appears to be responsible for dark, wrinkled, hard spots appearing on the grain.

The solutions to some of these problems were found in the use of a completely oxidized iron tan liquor; the employment of a small excess of the oxidizing agent in the liquor; the maintenance of iron in the ferric state by means of an after oxidation; the use of optimum basicity for tanning; and the careful neutralization of the pelt after tanning. All these will be dealt with at some length in the following sections.

The ferric sulphate in solution is unstable and liable to be decomposed by hydrolysis from a neutral or slightly alkaline solution, and is very rapidly precipitated upon the introduction of an alkali. Some attention has been devoted to investigating the possibility of correcting this tendency. The use of organic protective colloids, or of gums that form mucilages in water, or of substances that chemically combine with iron to prevent precipitation of ferric hydroxide from an alkaline solution, entails many complications. The difficulties in such cases are (1) that those nitrogenous protective colloids such as gelatine, egg albumin, blood albumin, etc., that are extensively used in connection with the other parts of leather manufacture are themselves coagulated by the highly concentrated tan liquor; (2) that the poly-hydroxy alcohols* in the form of syrup glucose, gum dextrin, starch, etc., exert a more or less reducing action on the ferric iron in the liquor, and (3) that compounds like Rochelle salt that hold up the ferric iron in an alkaline solution yield no tannage.† Other gummy bodies such as Irish moss, gum arabic, gum tragacanth, etc., have hardly any effect. The presence of a chromic salt or an aluminum salt in the iron liquor yielding the corresponding hydroxide in an alkaline solution has some tendency to hold up

* Glycerine can be used and seems to yield a tannage giving a soft, red, transparent leather.

† This speaks strongly of the chemical theory of leather formation in iron tannage.

the precipitation of iron as ferric hydroxide and thus stabilizes it, especially when the amount present is equal to or greater than that of the iron, but this works best in a solution so alkaline as to peptize the chromic hydroxide or aluminium hydroxide.[30] To regulate the speed of precipitation and also of the tanning action of iron in the pelt there is, at present, no satisfactory way except by the careful adjustment of the basicity of the iron liquor and of the control in subsequent neutralization.

To minimize the interference of iron in the leather with dyeing, it is found that if the neutralized tanned pelt is first dried to "crust" before coloring, the iron appears better fixed in the fiber and its chemical activity greatly lessened. The use of pyrogallol tannins such as sumac, oak, etc., or certain less astringent catechol tannins such as mimosa, gambier, etc., then gives only a light grayish color so that these tannins can be used for mordanting as can also other vegetable matter such as fustic, etc., that do not produce a decided black with iron when used in small quantities. To keep the leather soft and flexible it is generally advisable to apply a somewhat heavy fat liquoring, or an oil re-tan using marine oils such as cod liver oil, shark liver oil, etc.

[30] Cf. "Hydrous Chromic Oxide" by C. F. Nagel, Jr., *Jour. Phys. Chem.*, Vol. 19, p. 331 (1915).

Also "On the Behavior of Some Oxides with Caustic Potash in the Presence of Oxide of Chromium" by Northcote and Church, Vol. 6, p. 54 (1853).

Section IX.. Chrome-Iron Joint Tannage.

This form of joint tannage from the use of sodium dichromate as the oxidizing agent for iron proved to be very successful. It did not give a pure iron tannage, but a joint tannage of the chrome as well as iron. The relative amount of tannage due to each in the resulting leather is dependent upon the relative quantity of each present in the liquor.

From the invention of the Augustus Schultz's two-bath chrome process, it has been established that a dichromate, or chromium in the hexavalent state, has little or no tanning property until after it is reduced to the chromic (trivalent) state, Cr^{+++}. It was seen* that ferrous iron had no tanning property until after it was oxidized to the ferric state. Considering the properties of the two salts it is evident that a combination of the two is a natural outcome, using one as the oxidizing agent and the other as the reducing agent, both being benefited by the reaction mutually engaged in so that a joint tannage results. From the chrome tannage point of view, the use of the ferrous salt as a reducing agent possesses some advantages over the other reducing agents such as sodium bisulphite, sodium thiosulphate, sulphurous acid, glucose, glycerine, etc. For, unlike these latter which generally leave inert substances in the bath after the reduction reaction and which contribute nothing beyond the reduction of the chromate,† the ferric salt formed from the reduction reaction of the ferrous salt can be utilized as a tanning agent in the same bath. From the iron tannage point of view, the choice of the dichromate as an oxidizing agent is prompted by many considerations. First, as an oxidizing agent its oxidation potential is high and the oxidation reaction rapid, proceeding to completion in the cold. Second, for its oxidation action it requires only a very low acidity‡ in the solution so that the basicity of the resulting iron liquor is completely under control. Third, the waste product from the oxidation reaction, namely, the chrome salt, is a valuable tanning agent which can contribute fully to its share in the resulting tannage. Fourth, the green color of the chrome tannage has the effect of

*Section 8, page 54, footnote.

† In case sodium thiosulphate is used as the reducing agent, the colloidal sulphur may contribute some tannage, and it gives a lighter color to the leather.

‡ Contrast the case where a chlorate is used as the oxidizing agent.

neutralizing the red-yellow color of the iron, yielding a product of a less pronounced color. One possible drawback in the use of iron as the reducing agent for the chromate might be that the quantity of the ferrous salt used is comparatively large (5½ parts of $FeSO_4.7H_2O$ to 1 part of $Na_2Cr_2O_7.2H_2O$ by weight) especially when the commercial copperas has been partially air-oxidized, and that the color of the product is somewhat darker (brownish) than when other reducing agents are used with the chromate (light green). But for a certain class of goods this is not objectionable, and advantage can well be taken of the lower cost of production. It is important that the basicity of the bath be carefully adjusted,* otherwise the bath may be either too acid for the chrome or too alkaline for the iron, so that joint tannage can not be brought about. In general, an amount of 66° Bé. sulphuric acid equal to from 30-35 per cent. of the copperas employed with a sufficient amount of the sodium dichromate for complete oxidation is found to work well.

The following procedure may illustrate the mode of tannage in actual tannery practice. The percentages given are all calculated on the basis of the weight of the drained, pickled pelt (sheepskins, calfskins, etc.). For convenience, the weight of the skins is taken as basis to figure the quantities used. By "gal. %" (gallons per cent.) is meant gallons of the liquid in question per 100 pounds of the skin. For goatskins a somewhat larger quantity should be taken, say 10-20 per cent. greater. The examples given apply to drum tanning.

	Per cent.
(1) Copperas ($FeSO_4.7H_2O$)	11
Salt (NaCl)	5
Sulphuric acid (66° Bé. H_2SO_4)	1½
Water for solution (total)	12 gal.

Drum pelt in the solution for ½ hour, then introduce a solution of

	Per cent.
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Water to dissolve	2 gal.

* Historically Hylten Cavalin came close to the process, but because of lack of proper adjustment for the acidity he failed to obtain a successful tannage (Section 2, page 73).

Drum for about 1½ hours. (See if all iron is oxidized.) Add very slowly in portions, preferably through the trunnion, a solution of

	Per cent.
Soda ash (Na_2CO_3)	4½
Water to dissolve	3 gal.

After all the alkali is in, drum for 10 minutes longer. (See if the pelt is neutralized.) Rinse. This gives a tannage more of the nature of the iron than the chrome. The following modification can also be employed, if desired.

	Per cent.
(II) Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Salt (NaCl)	5
Water for solution	12 gal.

Drum the pelt in the solution for ¾ hour. Add to the drum a solution of

	Per cent.
Copperas ($FeSO_4.7H_2O$)	12
Sulphuric acid (66° Bé. H_2SO_4)	2½
Water for solution	4 gal.

Drum for 1½ hours. (See that all chrome is reduced.) Run out excess spent liquor. Then introduce a suspension of

	Per cent.
Bleaching powder	1½
Water	3 gal.

Drum for 15 minutes. Introduce very slowly as before a solution of

	Per cent
Soda ash	3½
Water to dissolve	3 gal.

After all alkali is in, drum for 10 minutes longer. (See if the pelt is neutral.) Rinse. This gives a tannage more of the nature of chrome than iron.

(III) For one-bath tannage.

(a) When the liquor is to be prepared, take for each 100 pounds of the pelt

	Per cent.
Copperas ($FeSO_4.7H_2O$)	11
Sulphuric acid (66° Bé. H_2SO_4)	3
Salt (NaCl)	5
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	2¼
Water (total) for solution	15 gal.

(Add the dichromate very slowly when stirring. Use the liquor without unnecessary delay.)

(b) When a concentrated one-bath is already made according to the method of preparation given in Section 3, take

	Per cent.
Chrome-iron liquor (concentrated)	3 gal.
Water to dilute	12 gal.
Soda ash (Na_2CO_3) to neutralize	½

In either case, drum the pelt in the liquor for 1 to 1½ hours, or until the pelt is struck through.

Introduce very slowly as before

	Per cent.
Soda ash (Na_2CO_3)	5
Water to dissolve	4 gal.

After all the alkali is in, drum for 10 minutes longer. (See if the pelt is neutral.) Rinse.

The stock tanned by any of the above processes should be soft and full. It has a color varying from a dull yellow, grayish brown, to olive drab, depending upon the proportion of the chrome to the iron present. To secure the predominating effect of the chrome tannage, some chromic salt may be added to the liquor. The leather obtained does not stand boiling unless the chrome content is increased by the addition of a chromic salt to the liquor.

The leather can be dyed black with logwood with or without a "striker." It can be dyed with coal tar dyes, such as the acid, direct, and alizarine dyes. When it is to be dyed with a basic dye a mordant is required, in which case, the tanned stock is best first dried to "crust" and then wetted back for mordanting with fustic or other vegetable matter after which the basic dye is applied in the usual manner. For fat-liquoring a somewhat larger

quantity of the fat-liquor (5-8 per cent. of "sulphonated" cod liver oil, degras, "sulphonated" Neat's foot oil, or a commercially prepared mixture) can be used. The proper temperature for dyeing is between 130°-140° F. and that for fat-liquoring 110°-120° F.

The leather can be re-tanned in oil to advantage when cod liver oil or other fish oil may be used. It can be re-tanned and colored black in ordinary vegetable tannins. Some basic black can be used for topping. When a less astringent tannin is used, a light gray color is obtained. In such cases, drying to "crust" prior to the treatment is advisable.

A sample of sheepskin leather tanned according to (I) above gives the following analysis:

	Per cent.
Moisture	7.43
Ash	15.60
Fat	21.48
Fe_2O_3	10.51
Cr_2O_3	1.84
*P_2O_5	2.50
SO_3 (total)	2.12
Hide substance (N × 5.62)	43.85

* From some disodium phosphate introduced together with the alkali for neutralization.

Section X. Pure Iron Tannage.

As it is desired to determine the actual tanning value of a ferric salt, a considerable portion of the time has been devoted to the study of the pure iron tannage, that is to say, to the tannage where no other metals except iron that can yield a tannage are present. It has been often reported that iron tannage produces a brittle leather, a leather that draws together on drying, a leather that deteriorates on keeping, and so on. One of the arguments advanced is that iron in the leather acts as an oxygen carrier, taking in oxygen from the air and imparting it to the fiber, so that the fiber is gradually oxidized and corroded in the course of time.[31] It has so far not been found possible to confirm this report, but, on the other hand, there is sufficient evidence to show that any defect of this kind is due to an improper tannage rather than to the inherent nature of the tannage. For, when a leather is properly tanned, it is not at all brittle, does not draw together hard on drying, nor behave in any way different from other mineral tannage. Samples of sheepskin leather tanned with iron salts that have now been kept for more than ten months show no sign of deterioration of the sort reported. It is probable that these defects were brought about by the use of a too alkaline iron liquor in which ferric oxide had been caused to deposit on the surface, making the interior of the pelt impenetrable to the tanning agent. Too rapid a neutralization would also cause the same defect, as the ferric oxide which is caused to separate from the solution would coat the surface of the pelt. This gives rise to a hard outer layer (grain) and a wide soft zone underneath in the cross section of the pelt.

As it is the ferric iron that possesses the tanning property, it follows that all iron should be kept in the ferric state. It is not so much, however, to avoid a small loss of iron going to the ferrous state as to prevent the ferrous iron finding its way to the pelt causing irregularities in appearance and texture in the leather. Hence it is necessary to use a sufficient quantity of a proper oxidizing agent to bring about complete oxidation, and not only that, to use a small excess of the oxidizing agent (10-15 per cent.) to take care of any subsequent reduction. To insure this, a further guaranty is found in the introduction of a small quantity of

[31] "Die moderne Leder-Fabrikation" by Hermann Zeidler, p. 109 (1914).

a suitable oxidizing agent ($Na_2Cr_2O_7.2H_2O$, $CaClO.Cl$, etc.) toward the end of the tanning process, prior to the neutralization — the so-called after oxidation. This is a proper action at this stage, inasmuch as the oxidation reaction involves a decrease of hydrogen ion concentration in the solution, thus helping to fix the iron in the pelt.

The best basicity for the tan liquor is found to lie in a range varying between the ratio of 5 equivalents of the mineral acid radical (or radicals) present to every 6 equivalents of the ferric iron, and that of 3 equivalents of the mineral acid radical (or radicals) present to every 4 equivalents of the ferric iron. When much iron salt in the liquor is in the form of a sulphate, it is safer not to go too near the higher limit of basicity. For if such is the case a light yellow hydrated ferric oxide (not a red gelatinous ferric hydroxide) would then be thrown out on short standing. It is evident that the same danger of rapid precipitation exists during neutralization. Hence it is necessary to effect the neutralization very gradually. The total amount of an alkali needed for neutralization is only 70 80 per cent. of the theoretical.

For the oxidation of iron and the preparation of the tan liquor from a ferrous salt, chlorine is found to work very satisfactorily, as it can effect the oxidation in the cold in the absence of any acid and push the reaction to completion under a small pressure.* Other suitable methods of oxidation are those using nitric acid and sulphuric acid, and sodium nitrate and sulphuric acid. The latter is more economical because of the cheapness of the sodium nitrate (Chile saltpetre) employed. All methods involving the use of nitric acid in one form or another, however, require a boiling temperature, and hence a special container to resist the corrosive action of the hot nitric acid.

For tanning, a quantity of ferrous sulphate crystals, $FeSO_4.7H_2O$, between 12 and 15 per cent. of the weight of the drained pelt is generally sufficient, the higher figure being for heavy hides and for the goat skin. A rough guide to secure the correct basicity for tanning is to add 10 14 per cent. of soda ash, Na_2CO_3, of the weight of the ferrous sulphate crystals taken. This presumes that the ferric liquor to start with is neutral in composition.

* For detailed directions concerning the preparation of the tan liquor, see Section 3.

The following method for sheepskins in drum tanning can be used for illustration. Unless otherwise stated, all percentages are on the basis of the weight of the drained pelt. When the stock to be tanned is much below 100 pounds some judgment should be exercised in regard to the modification of these percentages.

	Per cent.
Iron liquor containing an amount of Fe_2O_3 equal to....	3½
(or as $FeSO_4.7H_2O$	12)
Salt, NaCl	4
Soda ash, Na_2CO_3	1½
Total volume for tanning	25 gal.

Drum for 1 to 1½ hours. Introduce into the drum a suspension containing

	Per cent.
Bleaching powder, CaClO.Cl	1¼
Water	1 gal.

Drum for 15 minutes longer. Neutralize the pelt very gradually (in small portions) with a solution of

	Per cent.
Soda ash, Na_2CO_3	4
Water to dissolve	3 gal.

After the alkali is all fed in, drum for 10 minutes longer. Rinse. Hang the tanned pelt to dry. Sammy back from "crust" and wet thoroughly for subsequent operations.

For a coloring black, use

	Per cent.
Hematine crystals	1½
Water to dissolve equal to twice the weight of the wet stock	

Make the solution alkaline with ammonia, and heat to 130° F. Drum for 30 minutes and then add to the drum a solution warmed to 130° F. containing

	Per cent.
Basic leather black	1
Water to dissolve	5 gal.

Drum for 20 minutes, or until the leather is colored through. Run off the spent dye liquor. Fat-liquor with an emulsion at 130° F. containing

	Per cent.
"Sulphonated" cod liver oil	6
Water	80

Drum for 45 minutes, or until all fat-liquor is taken up. Hang the fat-liquored stock to dry without setting out. Any commercial fat-liquor mixture can be used.

For such a black leather, however, a re tan in ordinary vegetable tannins is more economical and advantageous, since the vegetable tannin not only gives a black color but also a tannage to the leather. Consequently the leather obtained is fuller. For such purpose, use a tannin liquor, warmed to 110° F., containing, say,

	Per cent.
Quebracho liquid extract	15
Water	120

or a tannin liquor having a barkometer reading of from 15° to 20° Bk. Drum for 1½ to 2 hours. This generally gives a grayish black color. To obtain a deeper black color, top the leather with 1 per cent. basic leather black in the usual manner. This method of blacking dispenses with the logwood color and even with the "iron striker." For a light (silver) gray color, pyrogallol tannins, such as pure oakwood tannin, sumac, etc., or a less astringent catechol tannin, such as mimosa, gambier, etc., can be used. This vegetable re-tan, however, can best be carried out in a paddle.

In the case of heavy leather, an oil re-tan can be applied to advantage, using, say,

	Per cent.
Dégras	8
"Sulphonated" cod oil	4
Water	12 gal.

Drum for 1½ hours with the mixture warmed to 130° F. (At present shark liver oil is available and can be utilized for this oil re-tan.) Or, the leather may be stuffed with a mixture of stearin, tallow, and "sulphonated" cod oil, using, for example,

	Per cent
Stearin	4
Tallow	10
"Sulphonated" cod oil	8

Heat the fat mixture to 150° F. in the drum, and drum for about ½ hour.

In general, an iron tanned leather is tough, heavy, but somewhat harsh. Hence it is generally advantageous to give the leather a good far-liquoring, or oil stuffing, or oil re-tan. It does not resist a boiling temperature but begins to contract at about 170° F. or lower.

For dyeing the iron tanned leather with basic dyes, the remarks made in Sections 8 and 9 apply here with a greater force.

A sheepskin leather tanned with 8 per cent. $Fe_2(SO_4)_3$, 4 per cent. NaCl, and 1.6 per cent. Na_2CO_3, subsequently neutralized with 4½ per cent. $CaCO_3$, and finally lightly fat-liquored with a mixture of neat's foot oil and a mineral oil, gives the following analysis:

	Per cent.
Moisture	14.10
Fat	5.37
Ash	20.01
Fe_2O_3	4.08
SO_3 (total)	3.26
Hide substance	51.22 ($N \times 5.62$)

This sample of sheepskin leather is tough and full, but feels somewhat harsh. It has a beautiful yellow-red color. From the analysis of the iron content, it seems that an amount of iron as low as 4 per cent. Fe_2O_3 of the weight of the air-dried sample is sufficient to give a satisfactory tannage.

Calcium carbonate (or the "precipitated lime") or magnesium carbonate is found to be very suitable for neutralization in place of, or together with, soda ash. It is cheap and can be used in excess to prevent the presence of any free mineral acid (H_2SO_4) in the leather. The calcium or magnesium sulphate formed in the leather during neutralization, furthermore, serves to give weight to the leather.

It might also be mentioned that in a tannery where chrome or vegetable tannage is employed, the presence of an iron salt is incompatible with good appearance of leather and all possible care is to be taken to keep away any iron from all liquors. In iron tannage this difficulty disappears.

Section XI.—Iron Phosphate Tannage.

As the iron tanned leather has a pronounced red-yellow color and as iron is capable of forming many colored bodies both with the organic and inorganic substances, attention is naturally drawn to the utilization of this chemical activity of iron for coloring the leather by a treatment with a substance which combines with iron to give the color. At the same time, it should be equally possible to find a substance that will give with iron a color lighter than that of the iron leather itself. In general, these combinations are in the form of a precipitate. Thus, Knapp treated his iron leather with a fatty acid forming a yellow precipitate of "iron soap" in the leather.[82] He was not, however, so much concerned with the yellowish brown color of the "iron soap" as with the fixation of iron in the leather so that it could not be washed out. The use of potassium ferrocyanide solution for producing a blue color has been mentioned.[83] But it is found that the color is not fast and is gradually washed out, especially when the leather after such a treatment is not immediately fat liquored; and, if the pelt is treated with the ferrocyanide solution before the iron has been fixed in the leather, a very poor tannage is obtained. Logwood (for dull black color) and fustic (for green black color) coloring matters have been long known in their use with iron (as a "striker"); but while they give a fast color, they contribute no material tannage. And it is said that much excess of iron should be avoided as it would render the leather brittle and liable to crack.[84] A soluble sulphide or polysulphide has been advocated for making black leather in connection with the iron tannage by O. Rohm,[85] but there are grave doubts as to its practicability, because these alkaline or alkaline earth sulphides generally have a strong reducing action, and the black ferrous sulphide formed is merely a filler and not a tanning agent for the pelt.

It is found feasible, however, to make the black or grayish leather by re-tanning the iron leather in ordinary vegetable tannins. This not merely gives the color, but also involves a

[82] British Patent No. 2,716 (1861).
[83] "A Text Book of Tanning," by H. R. Procter, p. 222 (1885).
[84] "Leather Dressing," by M. C. Lamb, p. 149 (1907).
[85] British Patent No. 103,827 (1917).

further tanning action. The leather thus obtained partakes of the characteristics of both the mineral and the vegetable tannages.

A scheme of making a light colored, or substantially white leather with the use of a phosphate has been satisfactorily worked out. The function of the phosphate seems to be more than producing a yellowish white compound of ferric phosphate in the leather. Borax having a property of forming a light red compound, ferric borate, could be used, but the quantity needed is usually large. It is, however, suitable for neutralization because of its mild alkaline nature. It may be added that other white or yellowish white compounds of iron are the ferric arsenate, and the iodate. Certain features about these substances, such as the poisonous character, the cost, etc., make their use for leather making clearly impracticable.

The idea of using a phosphate in connection with the iron tannage was suggested by the fact that from the colloid chemistry point of view the phosphate ion, being a trivalent negative ion, should act favorably towards the fixation of iron in the pelt. The mode of procedure is illustrated by the processes given below:

I. The pelt to be tanned is drummed in the ferric iron liquor of the same character and basicity as for pure iron tannage* and treated in the same manner up to the neutralization of the pelt. For neutralization, use

	Per cent.
Sodium pyrophosphate, $Na_4P_2O_7.10H_2O$	4
Soda ash, Na_2CO_3	2¼
Water for solution	20

or

Trisodium phosphate, $Na_3PO_4.12H_2O$	6
Soda ash	1¼
Water, same as above	

Introduce the solution slowly in the usual manner. It is found better to introduce the carbonate together with the phosphate than to add the phosphate alone first. Pyrophosphate is preferred because of its high phosphate content for a given weight. Borax may be used together with the phosphate and the carbonate; in which case the amount of the latter used should be correspondingly decreased. This tannage gives a leather of a light color. Subsequent treatments given in Sections IX and X can be followed.

* See Section 10 on Pure Iron Tannage.

II. The phosphate may be directly added to the ferric tan liquor giving a fine milky suspension. In this case, the addition of the alkali to bring about the proper basicity for tanning should be omitted. For sheepskins in drum tanning, use

	Per cent.
Ferric salt (calculated as $Fe_2(SO_4)_3$)	9
Sodium pyrophosphate, $Na_4P_2O_7.10H_2O$	4
Total volume	15 gal.

Dissolve the pyrophosphate in a small quantity of water and add it to the ferric salt solution slowly with constant stirring. Having stirred thoroughly, introduce it immediately into the drum and tan the pelt for 3 to 5 hours, or until the pelt is thoroughly penetrated. Neutralize the pelt slowly with

	Per cent.
Soda ash, Na_2CO_3	3½
Water to dissolve	3 gal.

After all the alkali is fed in, rinse and hang to dry. This gives an especially white leather. The process is suitable for light stock, such as glove leather and the like. The penetration is somewhat slow, hence a longer drumming is needed. When dried, the leather is full and soft. It becomes velvety after staking and perching.

The leather can be finished by any of the usual treatments. In dyeing, with basic coal tar dyes, the ordinary precautions in connection with the use of vegetable mordants should be observed. As the leather does not resist a high temperature, it is important not to use a temperature above 140° F. in dyeing or fat-liquoring.

A sample of sheepskin leather treated in accordance with (II) above, but without neutralization or fat-liquoring, gives a soft and almost white leather. Its chemical analysis gives

	Per cent.
Moisture	11.48
Fat	11.75
Ash	12.23
Fe_2O_3	3.97
P_2O_5	2.32
SO_3 (total)	2.15
Hide substance (N × 5.62)	54.09

Here again it shows that about 4 per cent. of iron as Fe_2O_3 on the basis of the air-dried sample is sufficient to give a tannage for light skins.

Section XII.—Conclusions.

The character of the iron tannage seems to lie between that of the alum and that of the chrome tannage. Iron seems to yield a more permanent tannage (towards water) than alum, but like the alum tannage, iron tanned leather does not resist the boiling temperature of water. If we take the critical temperature as that at which the sample under water begins to shrink or to draw together under the influence of heat, that point generally lies between 160°-175° F. In the case of a re-tanned leather (in fish oils or vegetable tannins) a somewhat higher test may be obtained; but in no case can an iron-tanned leather stand boiling, unless considerable portion of the tannage is due to chrome as in the case of the chrome-iron joint tannage.

It has been often reported that iron-tanned leather produces a brittle grain, and rots on storing. To do justice to the iron tannage it must be declared that an iron-tanned leather, properly tanned, is not brittle on the grain and does not deteriorate on storage. Samples of the leather that have now been kept for more than ten months show no sign of deterioration. Sometimes the product obtained is somewhat stiff and "flat," but this should not be ascribed to the inherent properties of the tannage. The strength, the fullness, the elasticity are, in our opinion, a matter of proper tannage and not dependent upon the nature of the tannage.

As a considerable amount of salt (4-5 per cent. of the weight of the pelt) is needed in the liquor and much of it is formed from neutralization, it is important to rinse the tanned stock after neutralization to wash off most of the neutral salts present ($NaCl$, Na_2SO_4, etc.); otherwise their presence in the leather may cause dampness or even salt stains or spues. Iron tannage is much affected by the presence of grease or any imperfections in the skins, and when such is the case, unevenness of color and other irregularities are liable to show up on drying. Hence the necessity of uniform softening of the pelt and of degreasing.

Iron-tanned leather generally runs high in ash. The leather has oftentimes a harsh feel, due probably to the presence of a large amount of iron oxide (Fe_2O_3) in the leather. Because of the harsh feel it is generally advisable to give the leather a some-

what heavy fat liquoring or an oil treatment. The use of flour, egg yolk, etc., may be practiced, if desired. At the present stage of our knowledge it seems that to produce a satisfactory tannage at least for a light leather an amount of iron calculated as Fe_2O_3 not less than 4 per cent. of the weight of the air dried sample should be present.

The iron tanned leather compares favorably with other mineral tanned leather. The red-yellow or brown-red color of the tannage, however, is for some purposes an undesirable feature. The chemical activity of iron in the leather forming dark colored compounds in the leather is another drawback. But even with all these limitations, there is much to be said in its favor. There are certain classes of goods in which these features are of no consequence and the saving in the cost of production is very material. True, there are difficulties in connection with the tanning operation and subsequent treatment of the leather—difficulties which in other tannages either do not exist, or are less serious. But the process, like any other new process, necessitates a new set of conditions. To summarize, the following main factors may be mentioned:

I. Completeness in the oxidation of iron and maintenance in its ferric state by using an excess of a proper oxidizing agent, and by means of an after oxidation.

II. Adjustment of proper basicity by the addition of a proper amount of an alkali, a basicity between the ratio of one OH^- equivalent to every 5 equivalents of the mineral acid radical present, and that of one OH^- equivalent to every 3 equivalents of the mineral acid radical present, being the proper range for tanning.

III. Gradual neutralization to be effected so that iron may be uniformly fixed in the pelt throughout its thickness.

IV. Drying to the "crust" state before subsequent treatment to minimize the chemical reactions between the iron in the stock and the substances employed that would react with iron to give an undesirable color.

It should not be omitted to mention that the subject of iron tannage presents a broad unexplored field and that this study is far from being exhaustive. Other phases could have been taken up and it is hoped that this work will serve as an indication for much that remains to be done.

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Appendix.—A Tentative Procedure for the Ordinary Chemical Analysis of Iron-Tanned Leather.

With more new chemicals introduced in the manufacture of leather, the chemical analysis of the leather naturally becomes more complicated. The following is a proposed system of the chemical analysis for iron-tanned leather ordinarily sufficient for commercial work. With the exception of the determination of free mineral acid, all procedures here given have been tested and found to give satisfactory results. While there are but few features in these methods, the details of the procedure, and the quantities of the reagents to be taken, etc., are those actually found to work well. The determination of the free mineral acid is based on the Procter and Searle's method, and that of the hide substance is adapted from the Dyer's modification of the Kjeldahl method for nitrogen. In order to bring out certain points in the analysis more clearly, notes have been added to each procedure, based upon the results of observations in the laboratory. The order and the grouping of the determinations as found to be convenient are shown as follows:

(1) Moisture } in one sample
(2) Fat }

(3) Ash
(4) Fe_2O_3 } in one sample
(5) Cr_2O_3

(6) Free mineral acid
(7) P_2O_5 } in one sample
(8) SO_3 (total)

(9) Hide substance

When only isolated determinations are desired, this order, of course, need not be followed.

Sampling.—Leather to be analyzed should be reduced to small pieces of approximately uniform size. Heavy leather can be shaved with a planer and ground in a small mill. Light leather should be chipped or shredded to pieces of about ¼ inch long by 1/16 inch wide with the natural thickness of the skin. A composite sample should be made from different parts of the whole piece and the sample intimately mixed before a portion is taken for analysis. The prepared sample should be kept in a tightly stoppered bottle.

1. *Moisture.*—Weigh 8 grams of the air-dried sample into a tared glass dish and dry for 8 hours in an electric oven regulated at 99°-101° C. The loss in weight represents moisture.

$$\left(\text{Per cent. moisture} = 100 \times \frac{\text{loss in wt.}}{\text{wt. sample}}.\right)$$

NOTE 1.—The leather should not be exposed to a higher temperature or heated for an unnecessary length of time because any drying oil (cod liver oil, shark liver oil, etc.) used for fat-liquoring, oiling, stuffing, or re-tanning would be oxidized to a greater extent. This not only gives low result for moisture, but also for fat determination, as petroleum ether will not dissolve the oxidized fat.

NOTE 2.—The dried sample should be weighed rapidly as it quickly absorbs moisture from the air.

2. *Fat.*—Transfer the sample from the moisture determination to a Soxhlet extractor using petroleum ether (redistilled if necessary using distillate below 60° C.). Fill the dry, clean Soxhlet flask with 160-180 cubic centimeters petroleum ether (to about three-fourths full). Heat the flask in an electric heater (or over a water bath) for 8 hours after which distill the main portion of the ether from the flask into the thimble chamber, collecting this portion. Transfer the ether solution of the fat to a tared evaporating dish, evaporate off most of the ether over a steam bath, and dry the fat at 99°-101° C. in an electric oven for 2 hours. The content of the dish is fat.

$$\left(\text{Per cent. fat} = 100 \times \frac{\text{wt. of fat}}{\text{wt. sample}}.\right)$$

NOTE 1.—To prepare the thimble for extraction. wash the thimble (S. & S.) in a small portion of the ether. Line the bottom of this thimble with a tuft of absorbent cotton that has also been washed in the ether. Place the sample in the thimble and cover it with another tuft of the washed cotton. This size of the sample, together with the cotton lining and covering will be just comfortably contained in the thimble. The thimble prepared in this way will prevent any fine particles of leather from being sucked out through the bottom during syphoning, or from floating off the top when the thimble is completely covered by the ether. A piece of heavy glass tubing can be placed at the bottom of the chamber underneath the thimble to allow some clearance so that the ether can be completely drained from the thimble during syphoning. A small tuft of cotton may

be loosely placed at the opening of the condenser above.

NOTE 2. The same precaution in drying given in Note 1 under moisture determination applies here. When mineral oil is present in the fat extraction it is sometimes difficult to get a constant weight due probably to the mineral oil being constantly decomposed and volatilized off. The dried fat should also be weighed rapidly.

NOTE 3. There is only a trace of iron salt that is extracted from the leather by the ether.

3. *Ash.*—Weigh 2 grams of the air-dried sample in a tared platinum dish, platinum crucible, or porcelain crucible and heat first very gently and then to below dull-red heat. Stir the contents occasionally with a platinum wire and heat gently until it is thoroughly ashed. The residue is weighed as ash.

$$(\text{Per cent. ash} = 100 \times \frac{\text{wt. of ash}}{\text{wt. sample}}.)$$

NOTE 1. Chlorides of metals are likely to be partially volatilized and lost at a higher temperature. Sulphates of heavy metals are decomposed with the evolution of SO_3 fumes. If the sample is heated too strongly, especially at the beginning, the leather cakes together so that the inner part is difficult to burn off. Sometimes the content fuses when heat is applied too strongly, so that it is hardly possible to transfer the ash to a crucible for alkaline fusion. In this case it is better to use a platinum crucible for the ash determination. But when a phosphate is present, great care should be taken not to cause the reduction of the phosphorus with the result of ruining the platinum crucible.

NOTE 2. For iron-tanned leather a 2-gram sample is sufficient, as the ash usually runs high.

NOTE 3.—Owing to an inevitable loss of some chlorides and to an indefinite amount of sulphates decomposed, the significance of the ash determination cannot be of great value. Furthermore, unless the manner of heating and other conditions are the same, good checks in different hands are difficult.

4. *Iron.*—The ash from the last determination is fused in a platinum crucible with a well pulverized and intimately stirred mixture containing 1½ grams anhydrous pure K_2CO_3, 1½ grams anhydrous pure Na_2CO_3, and 1½ grams pure borax glass, until the liquid in the crucible appears homogeneous. Cool, meanwhile heating to boiling 150 cubic centimeters of distilled water in a

350 cubic centimeter casserole. Place the crucible in the hot water, cover the casserole with a watch glass, and boil very carefully. Wash out the contents of the crucible, break up the mass, and allow to settle. Filter by decantation, and wash the precipitate with hot water, collecting the filtrate in a 400 cubic centimeter beaker. Ignite the precipitate and weigh as Fe_2O_3.

$$(\text{Per cent. } Fe_2O_3 = 100 \times \frac{\text{wt. } Fe_2O_3}{\text{wt. sample}}.)$$

NOTE 1.—Only a trace of iron is found to pass into the filtrate. If desired, the precipitate on the filter can be dissolved with 20 cubic centimeters hot dilute HCl (1 conc. HCl : 2 water by vol.) and the ferric hydroxide precipitated again with NH_4OH with the addition of 2 grams NH_4Cl. Or, the iron in the HCl solution can be determined by the Zimmermann-Reinhardt volumetric method, taking care to oxidize off all organic matter with $KMnO_4$ before $SnCl_2$ reduction.

5. *Chromium.*—Cool the filtrate from the iron determination and make it up to 250 cubic centimeters. Pipette 100 cubic centimeters of the filtrate into a 500 cubic centimeter beaker. Dilute to about 200 cubic centimeters. Acidify with concentrated HCl and add 5 cubic centimeters in excess. Add 15 cubic centimeters of 15 per cent. KI solution and titrate with N/10 sodium thiosulphate solution, adding 1 cubic centimeter of thin, clear starch solution after the color of the solution has changed from red to light yellow. Titrate to the disappearance of the blue color.

$$(\text{Per cent. } Cr_2O_3 = 100 \times \frac{\text{cc. N/10 } Na_2S_2O_3 \times 0.002533}{\text{wt. sample}} \times 2.5).$$

NOTE 1.—When the chromium present is small, the orange color of the dichromate cannot be distinguished. Hence the acidification should be guided by a litmus paper.

NOTE 2.—A thin, clear starch solution that can keep for several months is prepared as follows: Take 1 gram ordinary starch powder and rub it into a paste with 25 cubic centimeters distilled water. Heat 200 cubic centimeters distilled water to boiling and stir the thin paste into the hot water. Boil for a few minutes when a transparent solution will be obtained. Filter the solution through absorbent cotton into a 250 cubic centimeter glass stoppered bottle. Add 5 cubic centimeters chloroform, stopper the bottle and shake.

NOTE 3.—When chromium in the iron tan liquor is to be deter-

mined, pipette 25 cubic centimeters of the sample in a 250 cubic centimeter graduated flask. Make up to the mark. Take 25 cubic centimeters and dilute to 35 cubic centimeters with distilled water. Oxidize the chromium with Na_2O_2 by adding small portions at a time with constant shaking; 1½ to 3 grams Na_2O_2 is sufficient for a sample containing 15 to 30 milligrams Cr_2O_3. After all the Na_2O_2 has been added, heat the solution until the volume remaining is about 10 cubic centimeters. Add 25 cubic centimeters distilled water and evaporate down to this same volume again. Dilute to about 150 cubic centimeters, bring to a boil, allow to settle and filter off the Fe_2O_3, collecting the filtrate in a 350 cubic centimeter beaker. Wash the precipitate with hot distilled water, collecting it with the filtrate. Determine chromium in the filtrate as before.[36] Ignite the precipitate and weigh as Fe_2O_3.

(Remark: Excess of Na_2O_2 used must be completely decomposed or a phenomena of the reappearance of the starch blue color shortly after it is discharged will occur, making the determination worthless.)[37]

6. *Free Mineral Acid* (Based on Procter and Searle's Method). —Weigh 2-gram sample in a platinum dish. Cover the sample with 25 cubic centimeters N/10 Na_2CO_3 (accurately titrated against the HCl used below). Allow the sample to wet thoroughly and evaporate to dryness on a water bath. Gently char the organic matter, cover with about 50 cubic centimeters hot distilled water, stir, and break up the mass. Filter into a 250 cubic centimeter beaker. Return the residue with the filter to the dish, and ignite gently. Cool and take up the ash with 25 cubic centimeters N/10 HCl. Filter into the previous filtrate and wash thoroughly. Add 1-2 drops methyl orange, and if red color is seen, titrate with N/10 alkali.

(Per cent. free mineral acid =

$$100 \cdot \frac{\text{cc. N/10 NaOH} \cdot 0.0049}{\text{wt. sample}} \text{ as } H_2SO_4.)$$

Note 1. This method has not been tested. A full discussion is found in "Leather Industries Laboratory Book" by H. R. Procter, pp. 367-73 (1919). From the experience with chrome leather analysis, we found that sometimes the color of the filtrate was so dark that it interfered with the methyl orange color in titration.

[36] See Section 4, p. 30, footnote.

[37] See "On the Volumetric Determination of Chromium in Chrome Leather" by Te-Pang Hou, Jour. Am. Lea. Chem. Assoc., p. 367 (1920).

7. *Phosphate.*—Ignite the residue from the last determination together with the filter paper in a platinum crucible. Fuse with 1 gram pure anhydrous K_2CO_3, 1 gram pure anhydrous Na_2CO_3, and 1 gram pure borax glass until the liquid appears homogeneous. Dissolve out the content of the crucible as described under iron determination above, filter and wash, combining the filtrate with the solution from the alkali titration for Free Mineral Acid. Acidify the solution slightly with HCl. Add 2 grams NH_4Cl and 15 cubic centimeters magnesia mixture and heat to boiling. Cool in ice water and add ammonia very slowly at first until the solution smells of ammonia on stirring. Add one-fifth of the volume of the solution of concentrated ammonia and allow to stand at room temperature for about 30 minutes. Filter by decantation and wash with water to which 2-3 per cent. ammonia has been added. Ignite the precipitate in a tared porcelain crucible first gently and then strongly with a blast burner or a large burner. Weigh as $Mg_2P_2O_7$.

$$(\text{Per cent. } P_2O_5 = 100 \times \frac{\text{wt. } Mg_2P_2O_7 \times 0.6376}{\text{wt. sample}}.)$$

NOTE 1.—It has been found that precipitating $MgNH_4PO_4$ in a hot solution gives a purer precipitate of this composition. See that a crystalline but not a milky precipitate results on the addition of ammonia.[25]

8. *Total Sulphate.*—Acidify the filtrate from the phosphate determination with concentrated HCl and add 5 cubic centimeters in excess. Boil to expel CO_2. Add 15 cubic centimeters N $BaCl_2$ solution very slowly with constant stirring. Allow to stand in a warm place for from 2 to 4 hours. Filter by decantation and wash thoroughly with hot water. Ignite and weigh as $BaSO_4$.

$$(\text{Per cent. } SO_3 = 100 \times \frac{\text{wt. } BaSO_4 \times 0.3429}{\text{wt. sample}}.)$$

NOTE 1.—The total sulphate determination by the alkaline treatment and fusion includes the free sulphuric acid (if any), the neutral sulphates, and the sulphate from the oxidation of sulphur in the protein substance (if no SO_3 is lost). With sufficient alkali present and with slow heating, no material amount of SO_3 should be volatilized during heating.

[25] Compare "Analytical Chemistry," Vol. II, by F. P. Treadwell, translated by Hall, p. 434 (1919).

NOTE 2.—If the total sulphate alone is to be determined the following method proves to be convenient and satisfactory.

Weigh a 2-gram air-dried sample in a platinum crucible, cover it with 15 cubic centimeters of N/5 Na_2CO_3 (approximately) and allow the sample to be thoroughly soaked in the alkali. Evaporate to dryness in an air bath (made by setting the crucible into a hole cut in a piece of asbestos board so that about one-fifth of the height of the crucible projects above the board, and placing the board with the crucible on an iron crucible of about 50 cubic centimeters capacity). When the sample is thoroughly dried, gently char it over a very low flame. Fuse the charred sample with 2½ grams K_2CO_3, 2½ grams Na_2CO_3, and 2½ grams borax (all chemically pure) after mixing them thoroughly. Dissolve out the mass as described above. (Fe_2O_3 can be determined here in the precipitate.) Acidify the filtrate with concentrated HCl, boil to expel CO_2 and determine SO_4= by $BaCl_2$ in the usual manner.

Remark: Other methods commonly recommended for the total sulphate determination are based on the destruction of the organic matter by oxidation with (1) fuming nitric acid (Stiasny's method), (2) chromic acid (a dichromate and concentrated H_2SO_4) and (3) sodium peroxide. With fuming nitric acid and chromic it is very difficult to bring the sample into solution even by a prolonged digestion. With the Na_2O_2 fusion, the method is more rapid, but it is accompanied with certain disadvantages. First, that an iron or a nickel crucible, in place of the platinum crucible, must be used and this interferes with the iron determination if it is to be made here; and second, that the frothing and spattering of the liquid during fusion is inevitable (unless the sample is first charred, in which case some SO_3 would be lost). The above method, as described, permits the use of the platinum crucible; gives a very quiet fusion yielding a low-fusing and non-viscous melt; and loses very little, if any, sulphur through volatilization during charring if sufficient alkali (Na_2CO_3) is present in the crucible. On the other hand, too much alkali will cause disintegration of the sample yielding a thick, frothing liquid which takes a long time to dry. The method is somewhat longer than the peroxide fusion.

9. *Hide Substance* (Adapted from Dyer Kjeldahl Method for the Nitrogen Determination). Weigh a 1 gram sample, wrap it in a small quantitative filter paper, and introduce it into a dry Kjeldahl flask (250 cubic centimeters capacity). Cover the sample with 25 cubic centimeters chemically pure 1.84 sulphuric

acid and place about 0.7 gram mercury or 0.9 gram solid $HgSO_4$ in the flask. Clamp the flask at an inclination of about 60° and heat very gently until no frothing is seen and the black liquid boils quickly. Cool and introduce 15 grams anhydrous Na_2SO_4 and three glass beads. Heat until the sample is completely dissolved and the color becomes light yellow. Cool completely and add very carefully about 150 cubic centimeters freshly distilled water, and shake until all is dissolved. Cool in running water. Transfer the solution to a 250 cubic centimeter graduated flask and make up to the mark. Pipette out 100 cubic centimeters into a 750 cubic centimeter R. B. flask, add ½ gram sodium sulphide crystals, $Na_2S.9H_2O$, dissolved in a little water, and allow to settle. Place in the flask three glass beads and three pieces of pumice stone. Make up the volume to about 300 cubic centimeters with freshly distilled water. Dissolve 10 grams NaOH in about 35 cubic centimeters water to which is added a small amount of rosolic acid. Pour the concentrated NaOH solution into the flask quietly down the side without disturbing. Connect the flask with a Hopkins distilling head to a Liebig condenser and distill with the delivery tubing dipped into the bottom of a 500 cubic centimeter Erlenmeyer flask containing 50 cubic centimeters N/10 HCl (accurately standardized), 50 cubic centimeters water and 1-2 drops methyl orange. Distill for about 45 minutes, when about 150 cubic centimeters of the water will have passed over. Titrate the excess of HCl with N/10 NaOH.

$$\text{(Per cent. hide substance} = 100 \times \frac{\text{cc. HCl used up} \times 0.00786}{\text{wt. sample}} \times 2.5\text{).}$$

NOTE 1.—Introducing the sample into the Kjeldahl flask by wrapping it first with a small quantitative filter paper prevents any fine particles of the sample from sticking to the upper part of the neck.

NOTE 2.—It is necessary not to introduce Na_2SO_4 into the flask until the frothing has completely subsided, otherwise, troublesome foaming on subsequent heating will result. With the above proportion of H_2SO_4 and Na_2SO_4 and with the catalytic effect of mercury, the sample will be brought into a complete solution in 20-30 minutes.

NOTE 3.—Mercury is first precipitated as grayish HgS in an acid solution, because it will react with NH_3 yielding the mercuric ammonia chloride precipitate $Hg.NH_2Cl$ from which NH_3 cannot be readily liberated. The precipitate of HgS does not interfere with the distillation, and quiet boiling prevails throughout. With NaOH introduced in the manner described, the heavier NaOH solution will remain at the bottom layer and there is no danger of loss of any ammonia before distillation. The presence of an excess of NaOH is indicated by the purple color of the rosolic acid.

NOTE 4.—The presence of much chloride in the sample will cause some loss of NH_3 during H_2SO_4—Na_2SO_4 digestion, as NH_4Cl is liable to volatilize off with strong heating.

VITA

Te-Pang Hou was born in August, 1890, in Foochow, China. He obtained his primary education in that locality and later in a Middle School in Foochow City.

In 1908 he entered the Railway Technical College, Shanghai, China, finishing his work in 1910. He was in engineering practice for some time with the Tientsin-Pukow Railway.

He came to the United States in the fall of 1913 and joined the Massachusetts Institute of Technology, Boston, Mass. There he took up Chemical Engineering, (Course X) and was later admitted to the new travelling course (Course X-A). He finished his work there in 1917, receiving the degree of Bachelor of Science.

From 1917-1918 he was on postgraduate work in applied leather chemistry at Pratt Institute, Brooklyn, N. Y. and received a certificate for the work in June, 1918. From 1918-1920 he was in the graduate school of Columbia University, New York, N. Y., where he received the degree of Master of Arts in June, 1919.